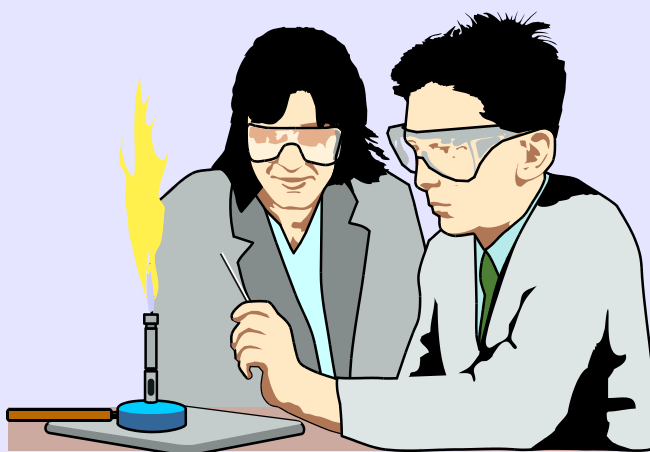


# Chemistry Practical Work

## Part I : Instructions



**Flame Test**

# Part I : Instructions

## List of Experimental Work

1. Titrimetric Analysis: The Determination of a Strong acid with Standard Sodium Hydroxide.
2. Titrimetric Analysis: Standardisation of Hydrochloric acid using Sodium Carbonate.
3. Titrimetric Analysis: Estimating the Relative Molecular Mass of an Unknown Acid.
4. Gravimetric Analysis: To Determine the % Water of Crystallisation in a Hydrated salt.
5. The Preparation and Properties of Chlorine.
6. Qualitative Analysis: Flame Test.
7. Further Qualitative Analysis: For Gases, Cations and Anions.
8. Measurement of Enthalpy Change when a Metal is Displaced from solution.
9. Chemical Kinetics Investigations: Effects of Concentration and Temperature.
10. Properties of Hydrocarbons.
11. Properties and Reactions of Alcohols.
12. Preparation of an Alkene by dehydration of an Alcohol.
13. Titrimetric Analysis:  
Using Permanganate to find the amount of Water of Crystallisation in an Iron salt.
14. Preparation of Iodoform.
15. Reactions and Properties of Organic Compounds. Mini Project.
16. Potentiometric Titrations.
17. Redox Reactions and Electrochemical Cells.
18. Electrolysis.
19. Qualitative Organic Analysis.
20. Analyse an aqueous solution of potassium chloride for chloride ion using a Back Titration method.
21. Investigating Transition Metals.

The first twelve experiments are considered suitable for a first year A-level chemistry course.

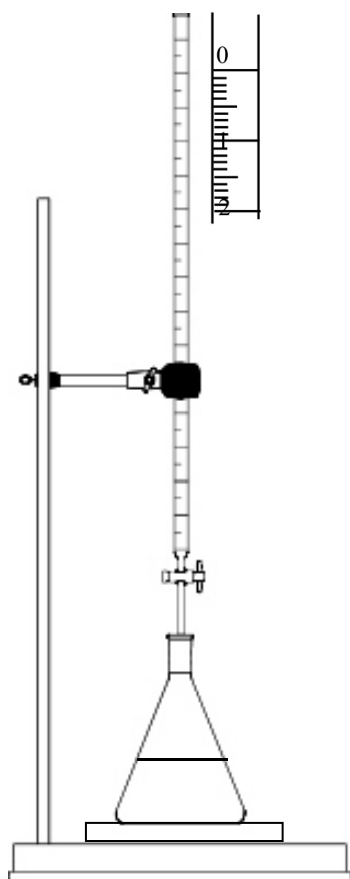
## Index

# Practical One

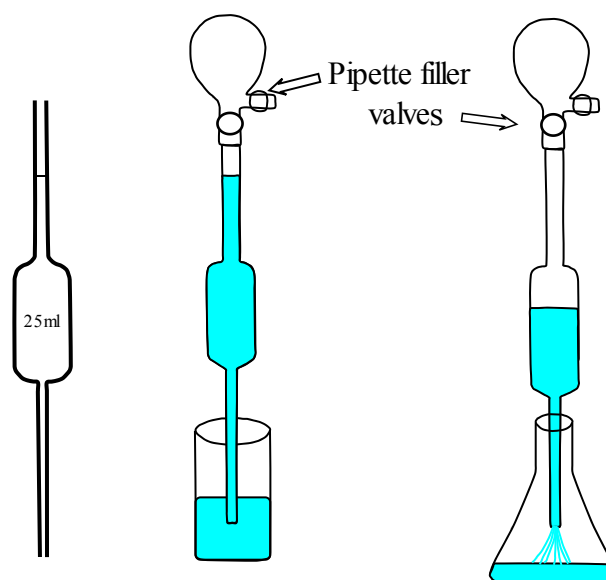
## Titrimetric Analysis (also called Volumetric Analysis)

### The Determination of a Strong acid with Standard Sodium Hydroxide.

Some of the equipment you will require for titrimetric analysis:



Burette and titration flask



Pipette and safety pipette filler

These are some of the indicators used in acid-base titration:

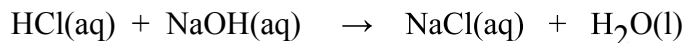
#### Colour changes of some common acid-base indicators

Indicator	In Acid	At neutralisation	In alkali
phenolphthalein	colourless	colourless	pink
methyl orange	pink	orange	yellow
methyl red	red	orange	yellow
screened methyl orange	red	grey	green

## Titrimetric Analysis.

### The Determination of a Strong acid with Standard Sodium Hydroxide.

You are provided with a solution of sodium hydroxide containing  $0.100 \text{ mol dm}^{-3}$ , and a solution of hydrochloric acid (a strong acid). We can assume that the acid and alkali react together quickly and completely in proportions given by the following chemical equation:



The reaction is not accompanied by any colour change, so we detect the exact point at which the number of moles of acid and base are equal (THE END POINT) with an indicator. Litmus, the best known indicator, is generally unsuitable for titrimetric analysis because its colour change is not sharp enough. However, most other indicators are suitable for titrations which involve a **strong** acid reacting with a **strong** base. The indicator used on this occasion is phenolphthalein which is colourless in acid and red in alkali.

#### Apparatus.

You may be provided with your apparatus, if not, obtain the following from storage:

a  $250 \text{ cm}^3$  conical flask, a  $25 \text{ cm}^3$  pipette, a  $50 \text{ cm}^3$  burette, a pipette filler, a burette stand (do not use ordinary metal bosses and clamps), a white tile, a wash bottle containing distilled water, a small plastic funnel (to fill the burette) and 2 x  $250 \text{ cm}^3$  beakers for collecting samples of solutions.

You will be required to rinse out glassware and use it more than once during experimental work. Use tap water and distilled water for this purpose. Take care not to cause splashing.

Use labels to identify sample solutions.

#### Procedures:

1. If the beakers are clean and dry, collect samples of the alkali and the acid. Do not take excessive amounts; make sure there is sufficient for the group. If the beakers are wet, rinse with the solution to be collected before you take it. Discard rinsings down the sink, then wash away from the sink with tap water.
2. Rinse the burette with the sodium hydroxide solution. Do this by placing the funnel in the top with the tap closed, and adding a  $5 - 10 \text{ cm}^3$  sample of the solution. Make sure the top of the funnel is not above your face, so that any inadvertent spillage does not get into your eyes round the edges of your safety spectacles. Run the liquid up and down the burette and discard it down the sink. Fill the burette in the same way, and clamp it carefully in the burette stand, placing the white tile on the base. There is no need to make the liquid level with the 0.00 mark, so long as the level is high enough (usually between 0.00 and 5.00). Make sure that the tip of the burette, below the tap, is also full of solution.
3. Place the pipette filler carefully on the pipette. Draw some acid into the pipette to rinse the inside and discard the rinsings into the sink. Fill the pipette to the mark and empty it into a conical flask. Touch the tip of the pipette to the surface of the liquid in the flask to transfer exactly  $25.00 \text{ cm}^3$  of acid. There is no need for the flask to be dry, providing it has been rinsed with distilled water before use. Dilution with water will not affect the titre, as the acid is measured by the pipette. To the liquid in the flask add 3 drops of the indicator. There will be no colour at this stage.
4. Read the bottom of the meniscus in the burette, record the value in a results table. Run alkali from the burette into the acid, swirling to mix the liquids. The end point is reached when the mixture takes on the first tinge of red which does not disappear on swirling. At intervals it may be helpful to wash down the sides of the flask with distilled water from a wash bottle to make sure everything in the flask is well mixed. Read the lower level in the burette, and record it in the table. Find the volume added by subtraction. Discard the liquid from the flask down the sink, and rinse out the flask, first with tap water, then with distilled water. Repeat the process until two consecutive titrations agree to within  $0.20 \text{ cm}^3$ . Reject any solutions in excess of requirements, rinsing them away down the sink. Rinse out all the apparatus you have used with tap water and return to the back bench near the main sink.

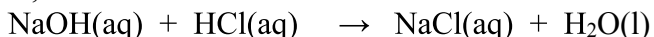


Calculate the mean of the best results, and use it as the volume of alkali required for the titration.

### Calculating the Molarity of the Hydrochloric acid

The balanced chemical equation is the first requirement

ie,



This shows that the acid and base react in a 1:1 molar ratio.

Let the concentration of the hydrochloric acid be expressed as  $M_1$  mole per  $\text{dm}^3$  (ie,  $\text{mol dm}^{-3}$ ) and let the volume be  $V_1 \text{ cm}^3$ .

Similarly, let the molarity of the sodium hydroxide solution be  $M_2$  mole per  $\text{dm}^3$  and the mean volume be  $V_2 \text{ cm}^3$ .

Then moles of sodium hydroxide used in the titration is,  $V_2 \cdot 10^{-3} \cdot M_2$ .

Since acid and base react in a 1:1 molar ratio this equals the moles of hydrochloric acid reacted.

Therefore,  $V_2 \cdot 10^{-3} \cdot M_2 = V_1 \cdot 10^{-3} \cdot M_1$

ie,  $V_2 \cdot M_2 = V_1 \cdot M_1$

from this  $M_1$  can be calculated since all the other values are known.

The concentration of the acid can be expressed in  $\text{g dm}^{-3}$  by multiplying  $M_1$  by  $36.5 \text{ g mol}^{-1}$  ( the molar mass of HCl ).

### Questions:

1. Name two other indicators suitable for this titration.
2. Can the acid be used in the burette rather than being pipetted into the titration flask? (ie, can the acid and alkali swap places?)
3. In your opinion, which step in the titration was likely to introduce the largest error in your result? Explain.
4. Before performing the titrations the glassware is rinsed following strict routines. Give reasons for adopting these routines.

# Practical Two

## Titrimetric Analysis: Standardisation of Hydrochloric acid using Sodium Carbonate

### PROCEDURE

#### **Safety:**

Wear safety spectacles at all times in the laboratory.

Acids and alkalis are caustic avoid skin contact. In the event of accidental contact wash the affected area thoroughly with plenty of cold, clean, water.

Take care when assembling and using glassware particularly when using glass pipettes. When applying pipette fillers hold the stem of the pipette near the end to which the filler is fitted. Ask for advice if in doubt. When introducing reagent (e.g., hydrochloric acid) into the burette use a plastic funnel and make sure the funnel is below eye level to avoid splashing reagent into your eye. Do **not** stand on a chair or stool to reach the top of the burette.

**If at any stage you are not sure what to do or how to proceed ask the teacher/lecturer in charge.**

To find the concentration of acid or alkali in a given solution it is convenient to compare the solution with another of accurately known concentration. Such a solution is known as a **standard solution**. In this experiment a standard solution of sodium carbonate will be prepared. Anhydrous sodium carbonate is a **primary standard**. Approximately M/10 hydrochloric acid solution will be titrated against the standard sodium carbonate solution thus allowing its concentration to be calculated accurately.

The end-point (or equivalence point) in the titration is judged using methyl orange indicator (yellow in alkali, red in acid).

Clean and rinse all glassware as previously described (check with the teacher/lecturer if you are unsure what to do).

Using a weighing scoop weigh out accurately between 1.30 & 1.50 g of dry, anhydrous, sodium carbonate; record this mass in your laboratory notebook. Transfer **the whole** of this to a 250 cm<sup>3</sup> volumetric flask. Approximately half fill the flask with distilled water, fit a stopper, gently shake the flask so as to completely dissolve the solid carbonate (it may dissolve slowly, be patient!). Make the solution up to the graduation mark with more distilled water. Mix thoroughly.

Fill a 50 cm<sup>3</sup> burette with hydrochloric acid (approximately 0.1M). Use a plastic funnel and fill to the 0.00 graduation mark. Check the reading again before you start the titration.

Introduce 25.00 cm<sup>3</sup> of the sodium carbonate solution into a clean 250 cm<sup>3</sup> conical flask. Measure out the carbonate solution using a 25 cm<sup>3</sup> pipette fitted with a pipette filler (**CARE**: check with the lecturer if you are not sure how to fit the filler **safely**).

Add 4 drops of methyl orange indicator and titrate against the acid until the solution acquires an orange-pink colour.

Record the burette reading in your laboratory notebook (the figure in the second decimal place must be a 0 or 5 showing that you are reading the burette to the nearest 0.05 cm<sup>3</sup>). Repeat the titration until you have at least **two** concordant readings which you are happy with (i.e., the two readings are the same within 0.05 cm<sup>3</sup>). During the titration the solution must be stirred by gently swirling the flask.

Rinse the glassware and return it carefully to the washing-up trolley.

### **Calculation**

1. Write the balanced equation for the reaction between sodium carbonate and hydrochloric acid.

2. How many moles of carbonate are contained in 25.00 cm<sup>3</sup> of solution?
3. How many moles of hydrochloric acid are required to react with the above moles of carbonate?
4. Using the mean titre as a measure of the volume of acid solution containing this number of mole, what is the molar concentration of the acid? What is the concentration of acid in g dm<sup>-3</sup>? Quote your final results to the appropriate number of significant figures.
5. If you are uncertain about these calculations consult the teacher/lecturer or try using the formula to find the molarity of the acid (ie,  $M_1 V_1/F_1 = M_2 V_2/F_2$ ).

# Practical Three

## Estimating the Relative Molecular Mass of an Unknown Acid

### Safety:

Wear safety spectacles at all times in the laboratory.

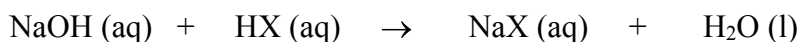
Acids and alkalis are caustic avoid skin contact. In the event of accidental contact wash the affected area thoroughly with plenty of cold, clean, water.

Take care when assembling and using glassware particularly when using glass pipettes. When applying pipette fillers hold the stem of the pipette near the end to which the filler is fitted. Ask for advice if in doubt. When introducing reagent into the burette use a plastic funnel and make sure the funnel is below eye level to avoid splashing reagent into your eye. Do **not** stand on a chair or stool to reach the top of the burette.

### **Introduction:**

Using titrimetric analysis find the relative molecular mass of the acid, HX (the acid used here is named at the end of the script!).

The acid reacts quantitatively with sodium hydroxide according to the equation shown below.



### **Procedure**

Assemble your equipment for titrimetric analysis.

Weigh accurately, into a clean scoop, 4.9 – 5.2 g of the acid HX. Record the accurate mass. Transfer the **whole** of this sample to a clean 250 cm<sup>3</sup> volumetric flask. Wash the sample from the scoop into the flask using distilled water from a wash bottle. Approximately half fill the flask with distilled water. Fit the flask with a stopper and gently shake to dissolve the solid. When the solid has **completely** dissolved, make up to the mark with distilled water. Shake the flask again to make sure the contents are thoroughly mixed.

Using a plastic funnel fill a clean burette with standard sodium hydroxide solution (**CARE**: avoid splashing this reagent on your skin!). Make a note of the exact concentration of this solution.

Transfer 25.00 cm<sup>3</sup> of the acid (HX) solution to a clean 250 cm<sup>3</sup> conical flask using a 25 cm<sup>3</sup> pipette (**CARE**: take the usual precautions when applying the filler to the pipette!). Add 2 or 3 drops of phenolphthalein indicator to the titration flask.

Place the flask under the burette and run alkali from the burette into the conical flask. Swirl the flask as this addition is made. When you are close to the end-point, add the alkali slowly and continue adding until the solution acquires a permanent pink tinge. If the solution is a definite red colour you have probably over-titrated (over-shot!) and you will need to repeat the titration more carefully.

Repeat the titration a number of times until you have concordant results.

### **Results:**

Enter your experimental data in the following table:

Mass of Acid (HX) taken:

Molarity of the sodium hydroxide:

Burette Readings:

1. Start:	Finish: Volume used:
2.. Start:	Finish: Volume used:
3. Start:	Finish: Volume used:
4. Start:	Finish: Volume used:

Mean Titre Value:

## Calculations

1. Calculate the molarity of the acid (HX) solution. Show your working in the space below:
2. Calculate the relative molecular mass of the acid (HX). Again, show your working:

## Conclusion:

**Question:**

Consider the experimental procedure and **list**, in order of importance, those operations which are most likely to introduce inaccuracy in the final result. Explain how these operations should be performed to keep the errors to a minimum.

(HX = potassium hydrogenphthalate, rmm 204)

# Practical Four

## To Determine the % Water of Crystallisation in a Hydrated salt.

### Safety note:

*Wear safety spectacles at all times in the laboratory.*

You will be heating a crucible using a bunsen flame. Take great care to keep the bunsen flame and hot surfaces (e.g., tripod, crucible and pipe-clay triangle) away from your skin. In the event of accidental contact, cool the affected area with lots of cold, clean, water from the tap.

Heat the crucible gently at first so as to avoid it cracking. Using suitable metal tongs handle the crucible carefully to avoid dropping it and spilling the contents. In the event of a breakage do not try picking up the pieces with your hands. When cool, use tongs and a dustpan and brush.

Keep all chemicals off your skin. In the event of accidental contact immediately wash the affected area with plenty of cold water.

If at any stage you are not sure what to do or how to proceed ask the lecturer in charge.

### Procedure:

Weigh a clean dry crucible and lid. Record the mass in your note book.

Half fill the crucible with hydrated salt (choose one from those provided – copper(II) sulphate is a possibility). Make sure the salt crystals are small. Weigh again. Record the mass. Place the crucible on a pipe-clay triangle, on a tripod. Arrange the lid so that there is a small space between the lid and the crucible so that water vapour can escape during the heating stage.

Heat the crucible gently with a small bunsen flame, moving the bunsen under the crucible. Then heat more strongly, but never let the crucible become too hot (do **not** allow it to get red hot). Arrange for the bunsen flame to just touch the crucible during the heating. Excessive heating may produce acidic fumes (eg, containing toxic oxides of sulphur).

Continue heating for about 15 minutes when a white powder remains. Remove the flame, place the lid to cover the crucible (**CARE**: still hot, use tongs).

Allow to cool to room temperature (ideally this cooling should occur in a desiccator – why?).

When cool weigh the crucible, lid and its contents. Record this mass in your note book.

Repeat the heating (for 5 minute intervals), cool and weigh. This is to ensure that the crucible has come to constant mass and all of the water of crystallisation has been removed.

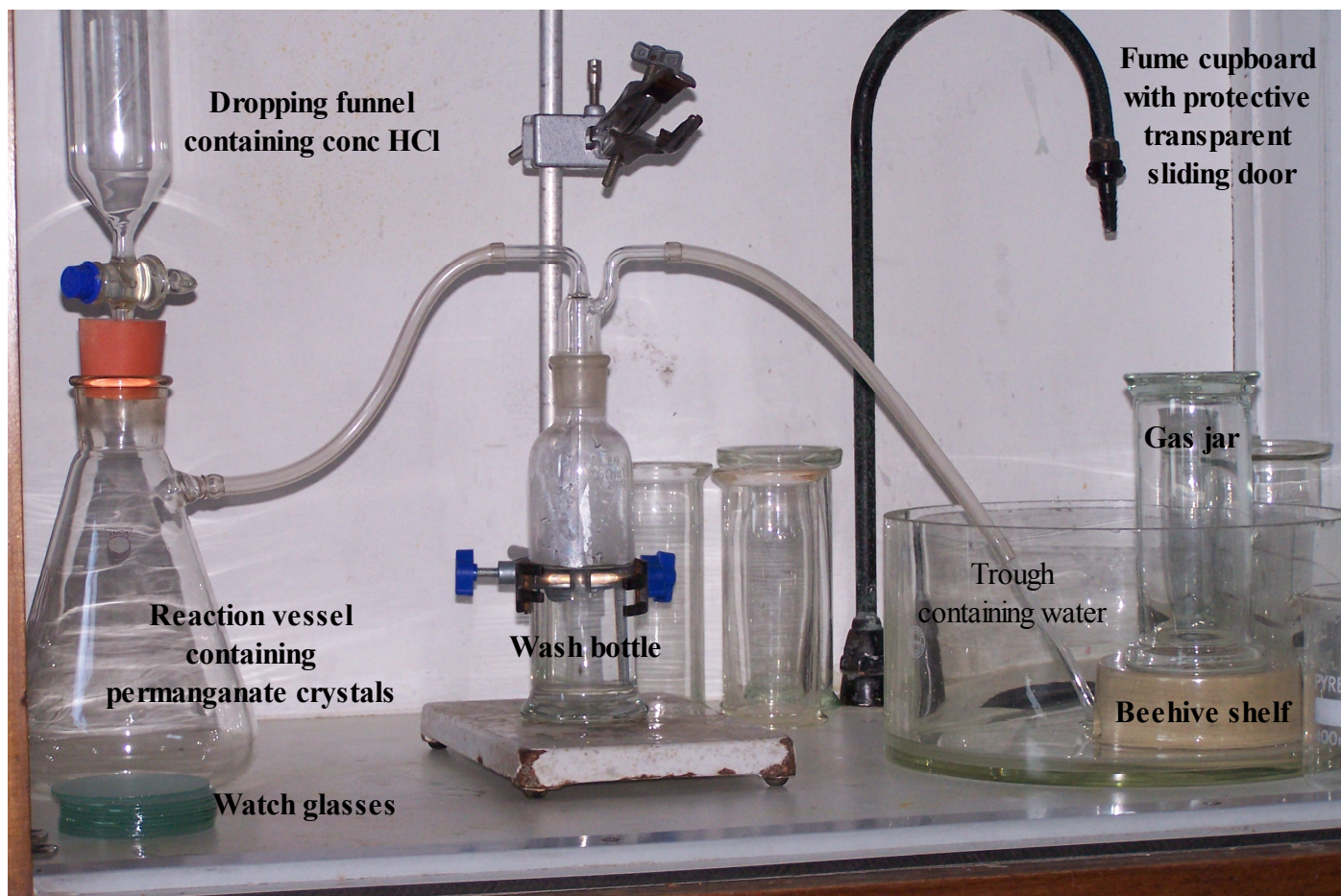
Before you discard the contents of your crucible record the appearance of the contents.

Very carefully add distilled water, dropwise (from a teat pipette), to the solid residue and make a note of any apparent changes. Explain these changes. From your results calculate the % water of crystallisation in the salt.

# Practical Five

## The Preparation and Properties of Chlorine

Some of the equipment which may be required for demonstrating the preparation & properties of chlorine:



Fill a few gas jars with chlorine using an apparatus similar to the above.

**Suggested investigations:**

Note **colour** of the gas.

Comment on the **density** of the gas. Ref. to weapon in the First World War.

**Solubility** in water. *Chlorine water*.

**Test** with damp litmus (blue and red).

**Test** with damp starch-iodide paper.

Shake with, (i) KBr & (ii) KI solutions

Burn a wax taper in the gas.

Introduce red hot iron wire into the gas.

Burn magnesium ribbon in the gas.

React with sodium metal.



Complete this table during the demonstration:

Tests & Reactions	Observations	Inferences/Formulae/Equations
Potassium permanganate & concentrated hydrochloric acid		$2\text{KMnO}_4(\text{s}) + 16\text{HCl}(\text{aq}) = 2\text{KCl}(\text{aq}) + 8\text{H}_2\text{O}(\text{l}) + 2\text{Cl}_2(\text{g}) + 5\text{MnCl}_2(\text{aq})$
colour		
smell	Pungent, choking, poisonous	Used extensively in which war?
density	About twice as dense as air	Will it form a layer above or below a layer of air?
Solubility in water	Slightly soluble	<p>Forms chlorine water. The solution contains, water, chlorine, hydrochloric acid &amp; hypochlorous (chloric(I) ) acid (HOCl).</p> $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCl}(\text{aq}) + \text{HOCl}(\text{aq})$
Test:Damp litmus paper		
Test: Damp starch-iodide paper		
Test: Shake with KBr (& KI) solution.		
<p>Action of Hydrocarbons (eg burning wax taper in jar of chlorine)</p> <p>Hold open mouth of conc ammonia bottle near mouth of gas jar.</p>		Which gas is indicated?
<p>Action of metals:</p> <p>Sodium</p> <p>Iron wire</p> <p>Magnesium ribbon</p>		$2\text{Na}(\text{s}) + \text{Cl}_2(\text{g}) = 2\text{NaCl}(\text{s})$ $\text{Mg}(\text{s}) + \text{Cl}_2(\text{g}) = \text{MgCl}_2(\text{s})$
<p>Action of alkali:</p> <p>Bubble chlorine into cold sodium hydroxide solution</p>	The gas is absorbed by the solution as a reaction occurs	$\text{Cl}_2(\text{g}) + 2\text{NaOH}(\text{aq}) = \text{NaCl}(\text{aq}) + \text{NaOCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ <p>A solution containing alkali and sodium hypochlorite (sodium chlorate(I) ) is sold as <b>bleach</b>.</p> <p>Write the ionic equation:</p>



# Practical Six

## Qualitative Analysis: Flame Test

### Analysis of Inorganic Compounds

Simple inorganic compounds are readily identified by applying a number of chemical tests. Sometimes these tests can be applied directly to the solid. Often, however, it is convenient to dissolve the solid in water (or occasionally, dilute acid), before applying the test.

#### 1. Flame test.

The flame test can be applied either directly, to the solid compound, or to its aqueous solution. The test is used to identify certain metals which give characteristic colours when their compounds are heated strongly in a bunsen flame.

Metal	Flame Colour
lithium	Red or magenta
sodium	Brilliant & persistent yellow
potassium	lilac
calcium	Brick-red (green through cobalt glass)
strontium	Crimson red (green through cobalt glass)
lead	Bluish-white
copper	green
barium	Pale green or apple green

The flame test is applied by dipping a clean platinum wire into an aqueous solution of the metal compound (or a sample of the powdered solid) and then heating the wire for a few seconds, in the hottest part of a bunsen flame (ie., just above the tip of the blue cone).

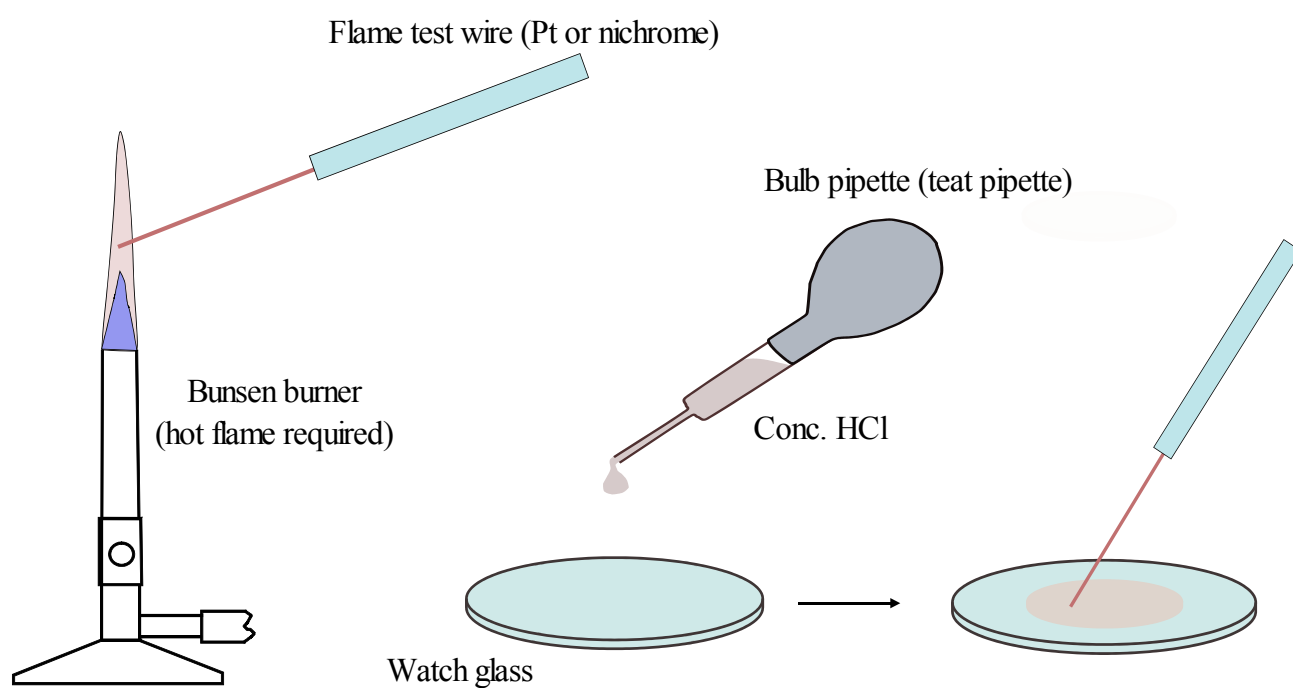
After applying the test the wire is cleaned by repeatedly dipping it in concentrated hydrochloric acid and heating until all of the residue has volatilised and the bunsen flame is pale blue.

*Perform this cleaning with the materials in a fume cupboard so as to avoid breathing HCl fumes.*

The equipment is illustrated on the next page.

Your teacher will provide samples on which to perform the flame test. Record details of the test and observations and inferences in a results table.

You will require the following equipment & samples of suitable compounds to test.



Clean the wire in a fume cupboard because conc. HCl gives off acidic, toxic, fumes

# Practical Seven

## Further Qualitative Analysis

In the previous theme we used the flame test to identify selected metal ions in their salts. We can now extend our analysis to include identification of gases and various cations and anions in aqueous solution.

Tests for gases  
Tests for cations-I  
Tests for cations-II  
Tests for anions-I

You will need to apply these tests on a selection of known and unknown substances so that you become familiar with the tests and observations. When you carry out this type of practical work you must record brief details of the tests. Observations should be recorded in more detail. It is normal practice to tabulate your results under 3 headings, TEST, OBSERVATION and INFERENCE (Conclusion). Your teacher will explain this to you.

GCE assessment normally involves an external practical exam or continuous practical assessment. Qualitative analysis exercises are very popular and in most cases you are required to tabulate your results.

### Tests for Gases and Vapours

Gas/vapour	Colour/odour	Test	Result
<b>Hydrogen</b> ( $H_2$ )	Colourless, odourless	Apply light splint	Burns with a blue flame, may explode ('pop')
<b>Oxygen</b> ( $O_2$ )	Colourless, odourless	Apply a glowing splint.	Re-lights glowing splint (or the splint glows much brighter)
<b>Water vapour</b> ( $H_2O$ )	Colourless, odourless	Readily condenses on cool surface of tube. Expose the vapour to dry cobalt(II) chloride vapour.	Colourless liquid (water).  Paper changes colour from blue to pink.
<b>Carbon dioxide</b> ( $CO_2$ )	Colourless, odourless.	Bubble through lime water.	Solution turns milky. Continued passage of gas through the mixture clears the solution.
<b>Ammonia</b> ( $NH_3$ )	Colourless, characteristically pungent.	Damp red litmus paper. Dip a glass rod in concentrated hydrochloric acid, so as to just wet the end of the rod with the acid, and hold it close to the source of the ammonia.	Turns blue.  Dense white fumes of ammonium chloride.
<b>Sulphur dioxide</b> ( $SO_2$ )	Colourless, pungent and choking.	Damp blue litmus paper. Bubble the gas into, (i) potassium permanganate solution acidified with dilute sulphuric acid. (ii) potassium dichromate solution acidified with dilute sulphuric acid.	Turns red.  Turns from purple to colourless.  Turns from yellow-orange to green.

Tests for gases and vapours (continued)			
<b>Nitrogen(IV) oxide</b> ( $\text{NO}_2$ )	Brown, pungent.	Bubble into freshly made iron(II) sulphate solution.	Brown colouration due to the formation of $\text{Fe}(\text{NO})^{2+}$ complex.
<b>Chlorine</b> ( $\text{Cl}_2$ )	Pale greenish-yellow, choking, poisonous.	Damp litmus.  Bubble through potassium bromide solution.	Bleached.  Yellow-orange colouration due to bromine.
<b>Hydrogen sulphide</b> ( $\text{H}_2\text{S}$ )	Colourless, bad egg smell, poisonous.	Moist lead(II) acetate paper.	Turns black.
<b>Hydrogen chloride</b> ( $\text{HCl}$ )	Colourless, pungent.	Damp blue litmus.  Gently blow across mouth of test-tube.  Bring glass rod, wetted with ammonia solution, to mouth of test-tube.	Turns red.  Misty fumes.  White fumes of ammonium chloride.



### Tests for Cations (positively charged ions) in aqueous solution.

Cation	Test	Result
<b>Hydrogen ion, <math>H^+(aq)</math></b>	(1) Spot the solution onto blue litmus paper.	Paper turns <b>red</b> if acid (& $H^+$ ions) present.
	(2) Add a small piece of magnesium ribbon.	Hydrogen gas evolved. Pops when ignited in air
<b>Calcium ion, <math>Ca^{2+}(aq)</math></b>	(1) Add dilute sodium hydroxide solution.	A slight white precipitate of calcium hydroxide. Insoluble in excess.
	(2) Add ammonium carbonate solution.	A white precipitate of calcium carbonate. Insoluble in excess.
eg., $CaCl_2(aq) + 2NaOH(aq) \rightarrow Ca(OH)_2(s) + 2NaCl(aq)$ $Ca^{2+}(aq) + 2OH^-(aq) \rightarrow Ca(OH)_2(s)$ $CaCl_2(aq) + (NH_4)_2CO_3(aq) \rightarrow CaCO_3(s) + 2NH_4Cl(aq)$ $Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$		
<b>Magnesium ion, <math>Mg^{2+}(aq)</math></b>	(1) Add dilute sodium hydroxide solution.	White, sparingly soluble, precipitate of magnesium hydroxide. Insoluble in excess.
	(2) Add dilute ammonia solution (sometimes called ammonium hydroxide solution)	Slight white precipitate of magnesium hydroxide. Insoluble in excess.
	(3) Add dilute ammonia solution, ammonium chloride solution and disodium hydrogenphosphate solution.	White precipitate of magnesium ammonium phosphate (may form slowly).
eg., $MgSO_4(aq) + 2NaOH(aq) \rightarrow Mg(OH)_2(s) + Na_2SO_4(aq)$ $MgSO_4(aq) + 2NH_4OH(aq) \rightarrow Mg(OH)_2(s) + (NH_4)_2SO_4(aq)$ $Mg^{2+}(aq) + 2OH^-(aq) \rightarrow Mg(OH)_2(s)$ $Mg^{2+}(aq) + HPO_4^{2-}(aq) + NH_3(aq) \rightarrow MgNH_4PO_4(s)$		
<b>Barium ion, <math>Ba^{2+}(aq)</math></b>	(1) Add dilute sulphuric acid.	White, sparingly soluble, precipitate of barium sulphate
	(2) Add dilute potassium chromate solution.	Yellow precipitate of barium chromate.
eg., $BaCl_2(aq) + H_2SO_4(aq) \rightarrow BaSO_4(s) + 2HCl(aq)$ $BaCl_2(aq) + K_2CrO_4(aq) \rightarrow BaCrO_4(s) + 2KCl(aq)$ $Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$ $Ba^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow BaCrO_4(s)$		



Cation	Test	Result
<b>Ammonium ion,</b> $\text{NH}_4^+(\text{aq})$	<i>Add sodium hydroxide solution.</i>	<i>Identify liberated ammonia gas. It has a characteristic pungent smell and turns damp, red, litmus blue. It also produces white fumes (of ammonium chloride) with hydrogen chloride gas (from the mouth of the concentrated hydrochloric acid bottle (in fume cupboard)).</i>
e.g., $\text{NH}_4\text{Cl}(\text{s}) + \text{NaOH}(\text{aq}) \rightarrow \text{NH}_3(\text{g}) + \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$ $\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{l})$		



## Tests for Cations (positively charged ions) in aqueous solution.

Cation	Test	Result
<b>Iron(II) ion, <math>\text{Fe}^{2+}(\text{aq})</math></b>	(1) Colour	Solids and solutions are often pale green.
	(2) Add dilute sodium hydroxide to a solution of the salt.	A muddy-green precipitate indicates iron(II) hydroxide. Insoluble in excess. Dilute ammonia solution gives the same result.
eg., $\text{FeSO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Fe}(\text{OH})_2(\text{s}) + \text{Na}_2\text{SO}_4(\text{aq})$ $\text{Fe}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Fe}(\text{OH})_2(\text{s})$		
<b>Zinc ion, <math>\text{Zn}^{2+}(\text{aq})</math></b>	(1) Colour	Solids and solutions are colourless.
	(2) Add dilute sodium hydroxide to a solution of the salt.	A white precipitate of zinc hydroxide. This is soluble in excess alkali.
	(3) Add dilute ammonia solution.	A white precipitate of the hydroxide. Dissolves in excess forming a complex ion.
eg., $\text{ZnSO}_4(\text{aq}) + 2\text{NaOH}(\text{aq}) \rightarrow \text{Zn}(\text{OH})_2(\text{s}) + \text{Na}_2\text{SO}_4(\text{aq})$ $\text{Zn}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Zn}(\text{OH})_2(\text{s})$ $\text{Zn}(\text{OH})_2(\text{s}) + 2\text{OH}^-(\text{aq}) \rightarrow \text{Zn}(\text{OH})_4^{2-}(\text{aq})$ (soluble zincate) $\text{Zn}(\text{OH})_2(\text{s}) + 4\text{NH}_3(\text{aq}) \rightarrow [\text{Zn}(\text{NH}_3)_4]^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq})$		
<b>Aluminium ion, <math>\text{Al}^{3+}(\text{aq})</math></b>	(1) Add dilute sodium hydroxide solution.	White, gelatinous, precipitate of aluminium hydroxide. Soluble in excess alkali.
	(2) Add dilute ammonium hydroxide solution.	White precipitate of aluminium hydroxide. Insoluble in excess reagent.
eg., $\text{AlCl}_3(\text{aq}) + 3\text{NaOH}(\text{aq}) \rightarrow \text{Al}(\text{OH})_3(\text{s}) + 3\text{NaCl}(\text{aq})$ $\text{Al}^{3+}(\text{aq}) + 3\text{OH}^-(\text{aq}) \rightarrow \text{Al}(\text{OH})_3(\text{s})$ $\text{Al}(\text{OH})_3(\text{s}) + \text{OH}^-(\text{aq}) \rightarrow \text{Al}(\text{OH})_4^-(\text{aq})$ (the aluminate ion)		



<b>Lead (<math>\text{Pb}^{2+}(\text{aq})</math>)</b>  (colourless solution)	Add dilute sodium hydroxide. Continue adding until present in excess.  Add dilute potassium iodide.  Add dilute potassium chromate.	A white precipitate is formed which dissolves in excess alkali.  A yellow precipitate of lead(II) iodide is formed.  A yellow precipitate of lead chromate ( $\text{PbCrO}_4$ ) is formed.
Equations:		
<b>Chromium (<math>\text{Cr}^{3+}(\text{aq})</math>)</b>  (green solution)	Add dilute sodium hydroxide. Continue adding until in excess.	A grey-green precipitate of (hydrated $\text{Cr}_2\text{O}_3$ oxide) is formed which dissolves in excess alkali giving a dark green solution of chromite ( $\text{Cr}(\text{OH})_6^{3-}$ ).
<b>Copper (<math>\text{Cu}^{2+}(\text{aq})</math>)</b>  (blue solution)	Add dilute sodium hydroxide. Continue adding to excess.  Add a dilute solution of ammonia. Continue adding to excess.	A pale blue precipitate of copper(II) hydroxide is formed. This is insoluble in excess alkali.  Pale blue hydroxide is formed which dissolves in excess ammonia solution to give a dark blue solution containing $(\text{Cu}(\text{NH}_3)_4)^{2+}$ ions.



### Tests for Anions (negatively charged ions) in aqueous solution.

Anion	Test	Result
<b>1. Hydroxide ion (OH<sup>-</sup> (aq))</b> Sodium and potassium hydroxides are very soluble in water. Other metal hydroxides are slightly soluble or sparingly soluble.	(1) Add a little solid ammonium chloride and mix.  (2) Add a drop of the hydroxide solution to red litmus.	Ammonia gas is evolved. This has a pungent smell and turns damp red litmus blue.  The litmus turns blue.
eg., $\text{NaOH(aq)} + \text{NH}_4\text{Cl(s)} \rightarrow \text{NaCl(aq)} + \text{NH}_3\text{(g)} + \text{H}_2\text{O(l)}$ $\text{OH}^-\text{(aq)} + \text{NH}_4^+\text{(aq)} \rightarrow \text{NH}_3\text{(g)} + \text{H}_2\text{O(l)}$		
<b>2. Carbonate ion (CO<sub>3</sub><sup>2-</sup> (aq))</b> All carbonates except those of sodium and potassium are insoluble in water.	(1) Add dilute hydrochloric acid.  (2) Add dilute barium chloride solution.	Carbon dioxide evolved. Forms a milky white precipitate with lime-water.  White precipitate of barium carbonate. Soluble in dilute hydrochloric acid.
<b>3. Hydrogencarbonate ion, (HCO<sub>3</sub><sup>-</sup>(aq))</b> All hydrogencarbonates are soluble in water.	(1) Add dilute hydrochloric acid.  (2) Add dilute magnesium sulphate solution.	Carbon dioxide evolved. Turns lime water milky.  No precipitate until the solution is boiled, then magnesium carbonate is precipitated.
eg., $\text{CuCO}_3\text{(s)} + 2\text{HCl(aq)} \rightarrow \text{CuCl}_2\text{(aq)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$ $\text{CO}_3^{2-}\text{(aq)} + 2\text{H}^+\text{(aq)} \xrightarrow{\text{heat}} \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$ $2\text{NaHCO}_3\text{(aq)} + \text{MgSO}_4\text{(aq)} \rightarrow \text{MgCO}_3\text{(s)} + \text{Na}_2\text{SO}_4\text{(aq)} + \text{CO}_2\text{(g)} + \text{H}_2\text{O(l)}$		
<b>4. Sulphate (SO<sub>4</sub><sup>2-</sup>(aq))</b>  All soluble in water except those of lead, barium, calcium and strontium.	Add a dilute solution of barium chloride.	White precipitate of barium sulphate formed. Insoluble in dilute hydrochloric acid.
eg., $\text{Na}_2\text{SO}_4\text{(aq)} + \text{BaCl}_2\text{(aq)} \rightarrow \text{BaSO}_4\text{(s)} + 2\text{NaCl(aq)}$ $\text{SO}_4^{2-}\text{(aq)} + \text{Ba}^{2+}\text{(aq)} \rightarrow \text{BaSO}_4\text{(s)}$		



<p><b>5. Sulphite (<math>\text{SO}_3^{2-}(\text{aq})</math>)</b></p> <p>Alkali metal sulphites are soluble in water. Other metal sulphites are sparingly soluble.</p>	<p>Add a dilute solution of barium chloride.</p>	<p>A white precipitate of barium sulphite is formed. This is soluble in dilute hydrochloric acid with evolution of sulphur dioxide.</p>
<p>eg,  <math>\text{Na}_2\text{SO}_3(\text{aq}) + \text{BaCl}_2(\text{aq}) \rightarrow \text{BaSO}_3(\text{s}) + 2\text{NaCl}(\text{aq})</math>  <math>\text{BaSO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{BaCl}_2(\text{aq}) + \text{SO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})</math></p>		
<p><b>6. Hydrogensulphate (<math>\text{HSO}_4^-(\text{aq})</math>)</b></p> <p>All hydrogensulphates are soluble in water. Only those of the alkali metals and ammonia form solids.</p>	<p>(1) Add dilute hydrochloric acid and a dilute solution of barium chloride.</p> <p>(2) Add dilute sodium carbonate solution.</p> <p>(3) If the hydrogensulphate is a solid, heat a small amount gently in a test tube.</p>	<p>A white precipitate of barium sulphate is formed.</p> <p>Vigorous evolution of carbon dioxide (little or no evolution of gas with sulphates)</p> <p>Choking white fumes of sulphur trioxide (acidic to damp blue litmus).</p>
<p>eg,  <math>\text{HSO}_4^-(\text{aq}) + \text{Ba}^{2+}(\text{aq}) \rightarrow \text{BaSO}_4(\text{s}) + \text{H}^+(\text{aq})</math>  <math>\text{HSO}_4^-(\text{s}) \rightarrow \text{SO}_3(\text{g}) + \text{HO}^-</math></p>		
<p><b>7. Chloride (<math>\text{Cl}^-(\text{aq})</math>)</b></p> <p>All chlorides are soluble in water except those of lead, silver, bismuth, antimony, tin and copper(I)</p>	<p>Add some dilute nitric acid to acidify and then add a dilute solution of silver nitrate.</p>	<p>A white curdy precipitate of silver chloride is formed. This precipitate is insoluble in dilute nitric acid <i>but soluble in dilute ammonia solution.</i></p>
<p>eg,  <math>\text{NaCl}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow \text{AgCl}(\text{s}) + \text{NaNO}_3(\text{aq})</math>  <math>\text{Cl}^-(\text{aq}) + \text{Ag}^+(\text{aq}) \rightarrow \text{AgCl}(\text{s})</math></p>		



<p><b>8. Bromide (Br<sup>-</sup>(aq))</b></p> <p>All bromides are soluble in water except silver, lead, mercury and copper(I)</p>	<p>(1) Add dilute nitric acid to acidify then add dilute silver nitrate.</p> <p>(2) Add a little chlorine water (use this in the fume cupboard).</p>	<p>A pale yellow (or cream) precipitate of silver bromide is formed. This is insoluble in dilute nitric but partially soluble in dilute ammonia solution.</p> <p>The mixture turns a reddish-brown colour due to displaced bromine (dispose of this solution down the fume cupboard sink).</p>
<p>eg,</p> $\text{CaBr}_2(\text{aq}) + 2\text{AgNO}_3(\text{aq}) \rightarrow 2\text{AgBr}(\text{s}) + \text{Ca}(\text{NO}_3)_2(\text{aq})$ $\text{Br}^-(\text{aq}) + \text{Ag}^+(\text{aq}) \rightarrow \text{AgBr}(\text{s})$ $2\text{Br}^-(\text{aq}) + \text{Cl}_2(\text{g}) \rightarrow \text{Br}_2(\text{aq}) + 2\text{Cl}^-(\text{aq})$		
<p><b>9. Iodide (I<sup>-</sup>(aq))</b></p> <p>All iodides are soluble except silver, lead, mercury and copper(I).</p>	<p>(1) Acidify with dilute nitric acid and then add dilute silver nitrate.</p> <p>(2) Add 2 or 3 drops of chlorine water (use this in the fume cupboard).</p>	<p>A bright yellow precipitate of silver iodide is formed. This is insoluble in nitric acid and also insoluble in ammonia solution.</p> <p>Chlorine displaces iodine which colours the reaction mixture yellow or yellow-brown.</p>
<p>eg,</p> $\text{KI}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow \text{AgI}(\text{s}) + \text{KNO}_3(\text{aq})$ $\text{I}^-(\text{aq}) + \text{Ag}^+(\text{aq}) \rightarrow \text{AgI}(\text{s})$ $2\text{I}^-(\text{aq}) + \text{Cl}_2(\text{aq}) \rightarrow \text{I}_2(\text{aq}) + 2\text{I}^-(\text{aq})$		
<p><b>10. Nitrate (NO<sub>3</sub><sup>-</sup>(aq))</b></p> <p>All nitrates are soluble in water.</p>	<p>Add dilute sodium hydroxide to make alkaline and then add a little zinc or aluminium powder. Stir and <i>warm</i> (<b>not</b> boil) the mixture in a boiling tube.</p>	<p>Ammonia gas is evolved. This can be detected by smell (<b>caution!</b>) and with damp red litmus paper which turns blue in contact with the gas.</p>
$2\text{NO}_3^-(\text{aq}) + 10\text{OH}^-(\text{aq}) + 7\text{Zn}(\text{s}) \rightarrow 2\text{NH}_3(\text{g}) + 7\text{ZnO}_2^{2-}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$ <p style="text-align: center;">zincate ion</p>		



# Practical Eight

## Measurement of the Enthalpy Change when a metal is displaced from solution.

### Introduction:

When aqueous solutions of copper(II) salts are treated with more reactive metals, the copper is *displaced*. This means that the copper is precipitated as the more reactive metal dissolves. Such reactions are accompanied by enthalpy changes, which can be measured by measuring the *corrected temperature rise* and knowing the heat capacity of the system.

### Safety Note:

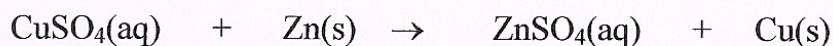
When using mercury thermometers, there is a risk of the escape of mercury if the thermometer is broken. Mercury is poisonous by skin contact and by inhalation of its vapour. Take care of the thermometer. If you do break it, ask for help from the laboratory staff: DO NOT TOUCH THE PIECES.

Copper(II) sulphate solution is toxic by mouth. If you accidentally get it on your skin wash it off immediately with plenty of cold water.

Zinc powder may ignite when heated. Keep it away from a naked flames and heat sources.

### Procedure:

The equation for the displacement reaction is;



Write the corresponding **ionic** equation

..... (2 marks)

Place the plastic cup inside the beaker so that it is well supported on your bench.

Measure 50 cm<sup>3</sup> of the copper(II) sulphate solution into the plastic cup using an appropriate measuring cylinder.

Weigh zinc powder (1.00g) into a test-tube. Place the test-tube in the copper sulphate solution.

Place the thermometer in the plastic cup and start the clock (ensure that the thermometer is properly supported and does not slide from the cup or unbalance the beaker). Record the temperature every half-minute until three readings have been taken. Use the table provided to record your results.

Time (seconds)	Temperature °C

(5)

At the next half-minute, do not record the temperature. Instead, pour the metal into the solution, and stir steadily and continuously until the time for the next reading.

Continue to record the temperature every half-minute for **five** more minutes.

Carefully discard the mixture into a suitable *residue container*, and rinse out the cup with tap water. Rinse the thermometer with tap water. Dry both carefully with paper tissues.

Repeat the experiment so as to give a second set of data.

Time (seconds)	Temperature °C



## Graphs and Calculation

Using the graph paper provided plot both sets of data. Plot temperature (vertical axis) against time. (8)

From your graphs find the *corrected temperature rise*.

For the first set of data: ..... (3)

For the second set of data: ..... (3)

Assume a value of 4.2 joules per degree per  $\text{cm}^3$  for the heat capacity of the reaction mixture.

Heat change (enthalpy change) = *corrected temperature rise*  $\times$  50  $\times$  4.2 joules = A

$A_1$  = ..... (3)

$A_2$  = ..... (3)

In both cases calculate the **heat change per mole of copper**:

1 = .....

..... (3)

2 = .....

..... (3)

Using these two values calculate the **mean** heat change per mole of copper:

..... (2)

The enthalpy change will be the negative of the above value (why?).

Express the result,

$\Delta H$  = .....  $\text{kJ mol}^{-1}$  (2)

Why is the test-tube containing the zinc placed in the copper sulphate solution?

.....

.....

..... (2)



Why are temperature readings taken before the zinc is added to the copper sulphate solution?

.....  
.....  
..... (2)

Explain the term, *corrected temperature rise*.

.....  
.....  
.....  
..... (2)

Comment on sources of error.

.....  
..... (2)

(Total = 50)

Please check that you have completed all of the activities and answered all of the questions.

Hand in this completed experiment script (with your graphs) for assessment.

**Name:**.....

**Date:**.....

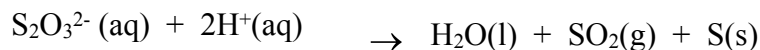


# Practical Nine

## Chemical Kinetics Investigations:

**(A ) To investigate the effect of concentration on the speed of reaction and to find the rate equation for a reaction.**

The reaction to be studied is that between thiosulphate and acid:



The reaction can be followed by noting the times for a **fixed** quantity of sulphur to appear.

(Thiosulphate ion resembles sulphate ion ( $\text{SO}_4^{2-}$ ) in which an oxygen atom has been replaced by a sulphur atom)

## Procedure

### Part I: Investigating thiosulphate concentration:

Using a 50 cm<sup>3</sup> measuring cylinder measure 50 cm<sup>3</sup> of 0.2M sodium thiosulphate solution into a clean 150 cm<sup>3</sup> or 250 cm<sup>3</sup> conical flask. Have ready, in a 10 cm<sup>3</sup> measuring cylinder, 10 cm<sup>3</sup> of 1M hydrochloric acid. (NB: Take care not to contaminate the thiosulphate solution with acid before the reaction is started)

Place the conical flask on a filter paper on which has been marked a cross. Add the 10 cm<sup>3</sup> of hydrochloric acid, starting the stop-clock immediately. Gently swirl the contents of the flask, and then allow the flask to remain still on the filter paper. Look vertically down through the solution at the cross and stop the stop-clock when the cross just disappears.

Rinse the flask immediately.

Measure into the flask 40 cm<sup>3</sup> of the 0.2M sodium thiosulphate and make up to 50 cm<sup>3</sup> with water (ie, add 10 cm<sup>3</sup> of distilled water). Repeat the above experiment using this 50 cm<sup>3</sup> of diluted sodium thiosulphate solution.

Repeat the experiment four more times using 30, 20, 15 and 10 cm<sup>3</sup> of sodium thiosulphate solution, making it up to 50 cm<sup>3</sup> with water each time.

### Part II: Investigating hydrogen ion concentration:

Repeat the experiment changing the hydrochloric acid concentration (& hence the hydrogen ion concentration). Keep the concentration of the thiosulphate constant (use 50 cm<sup>3</sup> of 0.2M solution) and vary the concentration of the hydrogen ion by using 9, 8, 7, 6 and 5 cm<sup>3</sup> of the 1M hydrochloric acid, making the volume of the acid up to a total of 10 cm<sup>3</sup> each time with distilled water.

## Interpretation:

Show how the time of reaction changes with concentration of reactants by plotting graphs of concentration against time. Also plot graphs of 1/Time against concentration (Note: 1/Time is proportional to **rate** of reaction). Explain what these graphs show. Deduce the rate equation for the reaction. Find a value for the rate constant (state units).

## **(B) Investigating the Effect of Temperature on the Rate of Chemical Reaction.**

The reaction to be investigated is that between sodium thiosulphate and hydrochloric acid. Represented ionically it is:



The progress of this reaction can be judged by noting how long it takes to precipitate a given amount of sulphur.

### **Procedure:**

Attach a strip of paper, marked with a dark ink cross or spot, to the side of a large beaker (eg, 1 litre). Fix the paper to the beaker with some adhesive tape so that it is about half-way up the side of the beaker. Two thirds fill the beaker with water and place it on a tripod and gauze so that it can be heated with a bunsen.

Clamp two boiling tubes (labelled A and B) vertically, inside the beaker so that they are halfway immersed in the water.

Position both the beaker and tube A so that the ink spot is on the opposite side of the beaker to the observer and can be seen through both the beaker and tube A.

Add 10 cm<sup>3</sup> of 0.1M sodium thiosulphate solution to tube A and 10 cm<sup>3</sup> of 0.5M hydrochloric acid to tube B. Allow the two solutions to come to thermal equilibrium with the surrounding water.

Obtain a stop-clock making sure that it works properly; set it at zero.

Add the acid from tube B to the thiosulphate in tube A and start the clock. Stir the mixture **gently** with a thermometer and note the steady temperature. Note also, the time taken for the ink spot to become completely obscured by the formation of colloidal sulphur.

Repeat the experiment at several temperatures (say, 10, 15, 20, 25, 30, 35, 40, 50 and 60°C). Use the same volumes and concentration of solutions as on the first occasion.

Tabulate your results.

### **Processing the results:**

Plot a graph of reciprocal time (ie, 1/time (seconds)) against temperature.

What effect does temperature have on the rate of reaction?

Can you say, from your results, that the rate of this reaction is directly proportional to temperature?

Plot another graph of log<sub>10</sub>(time) against the reciprocal of the absolute temperature (T K). What does this graph show? Use this graph to find the activation energy for the reaction.

# Practical Ten

## Properties of Hydrocarbon Compounds

Apply the following tests to an alkane, an alkene and an arene.

Hexane, cyclohexene and toluene (methylbenzene) are examples of compounds belonging to these groups of hydrocarbons. Tabulate your results.

### Safety

Wear eye protection ( safety spectacles or goggles).

Perform the reactions in a fume cupboard whenever possible. This is particularly important when substances are being combusted or when toxic gases or vapours are likely to be evolved.

**Never** heat organic solvents in open vessels, such as test tubes or beakers, using the naked flame provided by a bunsen burner. Always use the indirect heat provided by electric hot plates, electrically heated water baths or electric mantles. Electrical equipment must be flame proof; there must be no possibility of ignition due to sparks from the heating device.

Keep chemicals off your skin. In the event of accidental contact, the affected area must be washed immediately with copious amounts of cold, clean, water.

### (i) Combustion

**Perform this test in the fume cupboard.**

Carefully place a crucible lid, upside-down, on a pipe-clay triangle supported on a tripod. Add 3 drops of the hydrocarbon to the lid and ignite it with a lighted splint.

In your practical book record how readily the hydrocarbon ignites and the nature of the flame (i.e., how luminous and/or sooty).

If the flame is clean and not sooty it indicates that the hydrocarbon has a low carbon to hydrogen ratio (i.e., the carbon atoms have more-or-less their full quota of hydrogen). If a luminous, sooty, flame is produced it means the hydrocarbon is unsaturated to some degree and the carbon to hydrogen ratio is high (as in the case of aromatic hydrocarbons).

### (ii) Reaction with Potassium permanganate

Mix 1 cm<sup>3</sup> of the hydrocarbon with 2 cm<sup>3</sup> of 0.01M potassium permanganate and 2 cm<sup>3</sup> of dilute sulphuric acid. Mixing can be achieved by vibrating the tube or by fitting the tube with a stopper and inverting it a couple of times. If using a stopper allow for expansion and release the stopper immediately after mixing. Record any colour change.

Under these conditions potassium permanganate reacts with unsaturated hydrocarbons producing, in the case of alkenes, 1,2-diols; **the reagent is decolourised** and, often, a brown precipitate of manganese dioxide is produced.

Alkanes and arenes are generally resistant to this reagent under these conditions.

(Alkynes behave like alkenes, decolourising the reagent and being themselves converted to oxidation products.)

### (iii) Reaction with Halogen

**Measure out bromine solution in the fume cupboard; avoid skin contact and breathing the vapour since bromine is highly corrosive to the skin.**

Mix 1 cm<sup>3</sup> of the hydrocarbon with 3 cm<sup>3</sup> of 0.01M bromine in halogenated solvent (or *bromine water*). Record any colour change.

If there appears to be no reaction, place the tubes in a test-tube rack and stand this in daylight or ultra-violet light for a few minutes with occasional mixing. Record any changes.

Unsaturated hydrocarbons such as alkenes and alkynes, react readily with bromine producing the corresponding addition products; the **bromine solution is decolourised** in the process.

Alkanes react in the presence of ultra-violet light forming substitution products.

Arenes react in the presence of ultra-violet light or in the presence of halogen carriers; however, the products and mechanisms of reaction depend on the reaction conditions.

#### (iv) Reaction with Concentrated Sulphuric Acid:

**Concentrated sulphuric acid is extremely corrosive, take great care when applying this test.**

Introduce 1-2 cm<sup>3</sup> of concentrated sulphuric acid into a test-tube. Add dropwise, 0.5 - 1.0 cm<sup>3</sup> of the hydrocarbon. Stir the mixture with a glass rod and note any reaction.

(Dispose of the mixture by pouring it into a beaker of cold water & then pour the diluted solution down the fume cupboard sink)

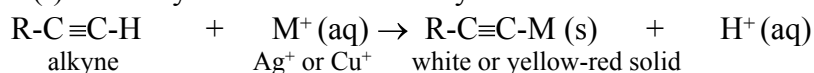
Unsaturated substances undergo addition reactions with concentrated sulphuric acid; heat is generated.

Sometimes there is discolouration of the reaction mixture. Arenes react much less readily at room temperatures. Alkanes do not react.

Having performed the above tests do you consider that it would be possible, using these simple tests, to distinguish arenes, alkenes and alkanes?

Explain your answer.

You may have wondered why we have not tested alkynes. The explanation is that, although generally little more reactive than alkenes, they are rather unpleasant smelling liquids. They exhibit the reactions of alkenes, however, if their molecules contain a terminal triple bond (i.e., one at the end of the hydrocarbon chain) they can be distinguished from the alkenes by their reactions with the transition elements, copper and silver. With solutions containing copper(I) ions they form yellow or red solid alkynides and with solutions containing silver(I) ions they form white solid alkynides.



Article: The sociable noble metal alkynides, D.E.F.Armstead, School Science Review, 1983, **65**, 332

# Practical Eleven

## Properties and reactions of Alcohols

### Safety note:

Wear safety spectacles and a laboratory coat at all times. Carry out a risk assessment.

Avoid breathing the vapours from organic compounds and use the fume cupboards when performing reactions which are known to produce toxic vapours. Ensure that the extractor fan to the fume cupboard is switched on.

Avoid skin contact with organic liquids and solutions of organic compounds. In the event of accidental skin contact wash the affected area with plenty of cold, clean, water. Methanol is toxic.

Many organic liquids and solvents are flammable. Never heat organic solvents using a naked flame (eg., bunsen flame); if necessary use an electrically heated water-bath.

Take great care when using acids and alkalis. Phosphorus pentachloride is corrosive.

### 1. Solubility

Introduce 2 cm<sup>3</sup> of distilled water into a test-tube. Add 2 cm<sup>3</sup> of methanol and gently swirl the tube (**Care:** Keep methanol off your skin and away from your eyes. It is toxic.).

Is methanol soluble in water? Is it insoluble, slightly soluble or very soluble?

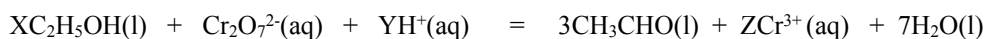
Test the solution with pH paper. Classify the alcohol as acidic, neutral or basic.

Repeat the test with ethanol (you may use industrial methylated spirit (IMS) which is about 95% ethanol).

### 1. Oxidation

Add 2 cm<sup>3</sup> of ethanol (you may use IMS) to a boiling tube. In another tube mix 1 cm<sup>3</sup> of potassium dichromate solution and 1 cm<sup>3</sup> of dilute sulphuric acid. Add this mixture to the ethanol in the first tube. Warm the boiling tube in a beaker of hot water (or electrically heated water bath). Swirl the contents of the tube periodically and inspect the reaction mixture. Note any colour change.

Ethanol is oxidised by the acid-dichromate. Complete the equation for the reaction and name the oxidation product. (replace X, Y and Z by appropriate numbers)



### 3. Phosphorus pentachloride (**Care:** corrosive and fumes in moist air)

Introduce 2 cm<sup>3</sup> of methanol into a boiling tube. Holding the tube in a holder, in the fume cupboard, carefully add a little (approx. 0.5g) phosphorus pentachloride. Note any reaction and test the vapour with a small piece of damp litmus paper (try both red and blue litmus). Also test the vapour with a strip of filter paper dampened with dilute ammonia solution. Record and interpret what you observe.

Write an equation for the reaction of methanol with PCl<sub>5</sub>.

### 4. Sodium (**Care:** sodium is a very reactive metal. Exercise care when using sodium. Use tweezers or spatula to move it and keep it off your skin.)

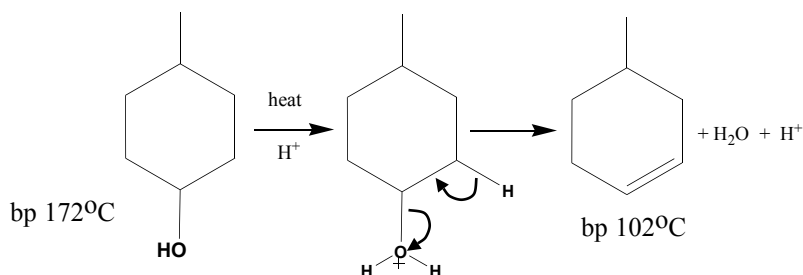
Introduce 4 cm<sup>3</sup> of methanol into a boiling tube. Add one small piece of sodium metal (a piece about half the size of dried pea; before adding to the alcohol, remove the coating of liquid paraffin by rolling the sodium over on a piece of dry filter paper). Return unused metal to the reagent bottle.

A gas is evolved. The gas is hydrogen. Write a chemical equation for the reaction.

# Practical Twelve

## Preparation of an Alkene by the Dehydration of an Alcohol

### Synthesis of 4-methylcyclohexene



### Safety:

(This preparation is provided as an alternative to the more usual cyclohexene because it gives less in the way of objectionable fumes!)

If you use a bunsen burner to heat the reaction vessel take great care to ensure that volatile, flammable, vapours do not make contact with the naked flame. Make sure all joints are well made. However, the apparatus must be vented to the atmosphere in the region of the receiver. Check your assembled apparatus with your teacher before using it.

A sand tray, under the flask, can be used to provide less direct heating although this reduces heating control. Electric mantles provide another method of heating. Ensure that the apparatus is adequately supported using stands and clamps.

Take care to avoid skin contact with hot surfaces & chemical reagents. In the event of accidental contact, cool and wash the affected area with copious amounts of cold water.

### Procedure:

Weigh into a 50 cm<sup>3</sup> pear-shaped flask 20g (22 cm<sup>3</sup>, 0.175 mol) of the alcohol, 4-methylcyclohexanol. Measured from a small cylinder, add 5 cm<sup>3</sup> of 80-90% phosphoric acid. Thoroughly mix the two reagents and add three or four antibump granules. Fit the flask with, still-head, thermometer, water condenser & vented receiver as for distillation. Make sure that all joints are well made (ie, no gaps between joints allowing flammable vapours to escape in the region of the bunsen flame) and heat the flask gently and slowly. When distillation begins do not allow the temperature to exceed about 95°C otherwise unreacted alcohol will distil over with the alkene. The distillation rate must be adjusted so that the alcohol has opportunity to be dehydrated.

Continue heating the flask until the distillation becomes very slow. At this stage the receiver will contain alkene and water probably as an emulsion; do not boil the distillation flask dry! Transfer the distillate (about 20 cm<sup>3</sup>) to a 250 cm<sup>3</sup> separating funnel and add 10 cm<sup>3</sup> of water. Mix the contents of the funnel and run off the bottom water layer.

Wash the remaining organic phase with 2 x 10 cm<sup>3</sup> of 10% sodium carbonate solution (**care**: allow for expansion due to evolution of carbon dioxide). Wash the organic phase, finally, with a little water.

Run the organic phase into a small beaker and add a few, small, granules of anhydrous calcium chloride. Leave to stand for a few minutes and decant and weigh your product. If necessary the product can be further purified by final distillation collecting in the range 101-103°C.

Calculate the % yield.

$$\% \text{ yield} = \frac{\text{actual yield in grams (or moles)}}{\text{maximum theoretical yield in grams (or moles) as deduced from the balanced equation}} \times 100$$

Consider your % yield and state reasons why it is less than 100%.

Test your product for **unsaturation** using, (a) dilute potassium permanganate, (b) dilute bromine solution.

Record the results and write formulae for the organic products.

# Practical Thirteen

## Using Permanganate to find the amount of Water of Crystallisation in an Iron salt.

### Safety:

Wear safety spectacles at all times in the laboratory.

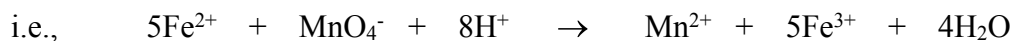
Acids are corrosive; avoid skin contact. In the event of accidental contact wash the affected area thoroughly with plenty of cold, clean, water.

Take care when assembling and using glassware particularly when using glass pipettes. When applying pipette fillers hold the stem of the pipette near the end to which the filler is fitted. Ask for advice if in doubt. When introducing reagent (e.g., oxidising agent such as permanganate) into the burette use a plastic funnel and make sure the funnel is below eye level to avoid splashing reagent into your eye. Do **not** stand on a chair or stool to reach the top of the burette. Permanganate solutions stain the skin; avoid skin contact. In the event of accidental contact wash the skin immediately with plenty of cold, clean, water.

Weigh accurately (2 places of decimals) about 6g of ammonium iron(II) sulphate into a large weighing scoop. Dissolve this solid in about 80 cm<sup>3</sup> of dilute sulphuric acid in a clean, graduated, 250.00 cm<sup>3</sup> volumetric flask. Make up to the mark with distilled water. Mix thoroughly.

Carefully introduce the permanganate solution (approx. 0.02M) into a clean burette. Introduce about 20 cm<sup>3</sup> of dilute sulphuric acid into a 250 cm<sup>3</sup> conical flask and add 25.00 cm<sup>3</sup> of the iron(II) solution from a clean pipette. Titrate this solution against the permanganate from the burette. Use the colour of the permanganate to judge the end-point; first permanent pink tinge. Repeat the titration until concordant results are obtained.

The permanganate reacts with iron(II) in a 1:5 ratio.



The exact molarity of the permanganate solution is known (ask for the value if it is not given). Calculate the molarity of the iron solution.

The iron salt has the formula,  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot x\text{H}_2\text{O}$ , find the value of  $x$ .

### Questions

1. In this experiment the iron is denoted iron(II). What does the (II) refer to?
2. Why is sulphuric acid required in this estimation?
3. Is ammonium iron(II) sulphate a primary standard? Explain.
4. The reaction is a redox reaction. Explain what this means referring to the various oxidation states of the reactants.

# Practical Fourteen

## Preparation of Iodoform (Tri-iodomethane, CHI<sub>3</sub>)

In this exercise iodoform is prepared from propanone (acetone). It can, however, be prepared from other compounds containing the CH<sub>3</sub>CO- group or indeed from alcohols which may be oxidised to provide the CH<sub>3</sub>CO- group.

The reaction, in which iodoform is produced, is used as a simple test for the above groups.

### Procedure.

Wear eye protection and laboratory coat. Carry out a risk assessment.

Dissolve 10g (0.06 mol) of potassium iodide in 25 cm<sup>3</sup> of distilled water in a 250 cm<sup>3</sup> conical flask and add 10 cm<sup>3</sup> of 2M sodium hydroxide (**CARE**: corrosive to the skin).

Now add 1.5 cm<sup>3</sup> (0.02 mol) of propanone from a small measuring cylinder. Rinse out the measuring cylinder with a little water and add the washings to the flask.

Cork the flask securely.

Support a 250 cm<sup>3</sup> dropping funnel in a ring or clamp on a retort stand. Introduce 40 cm<sup>3</sup> of hypochlorite (chloric(I) ) solution into the dropping funnel. (This bleach solution contains 12% available chlorine. **CARE**: corrosive to the skin.).

Carefully position the flask under the dropping funnel.

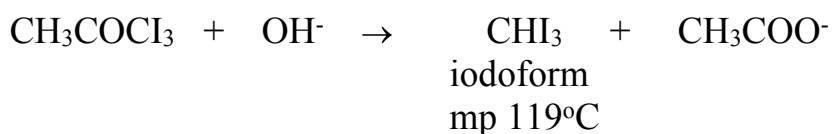
Remove the cork from the conical flask and allow the hypochlorite solution to *drop* in at a fairly rapid rate swirling the flask continuously. When all of the hypochlorite has been added cork the flask, mix thoroughly and allow to stand in the fume cupboard for about five minutes.

Filter under reduced pressure, wash the yellow crystals with a little water and drain thoroughly. Dry the crystals on a watch glass on a water-bath (*this must not be too hot otherwise the product will discolour and melt; if a number of samples are being dried at the same time the water bath should, preferably, be in a fume hood*).

Recrystallise from ethanol (IMS is satisfactory) and allow to air dry on a warm surface (preferably in a fume hood). Weigh your product.

Calculate the % yield based on the propanone used.

Equations:





# Practical Fifteen

## Reactions and Properties of Organic Compounds.

### CARBONYL COMPOUNDS

#### 1. Fehlings Reagent.

In a boiling tube mix equal volumes of Fehlings A and B (i.e., 2 cm<sup>3</sup> of each).

From a bottle in the fume cupboard, add 1 cm<sup>3</sup> of ethanal (acetaldehyde). Take care with this reagent it is volatile and flammable. Also it is an irritant and has a pungent smell. Use it in the fume cupboard. Swirl the mixture and then heat it by standing the tube in some hot water in a beaker, leave the mixture in hot water for 5-10 minutes. Record and explain the result. Do ketones react similarly? Try propanone (acetone) and record the result.

#### 2. Tollen's Reagent.

Introduce 2 cm<sup>3</sup> of dilute silver nitrate into a test-tube. Add one drop of dilute sodium hydroxide solution and swirl the tube, gently, to mix. Then add dilute ammonia solution, dropwise, with mixing until the grey precipitate just dissolves. This solution is known as Tollen's reagent; it gives a grey black precipitate, or a silver mirror, when treated with aldehyde. Add, to the reagent, 0.5 cm<sup>3</sup> of an aldehyde, such as ethanal (acetaldehyde), and mix. Record and explain the result. Do ketones react similarly? Try it with propanone (acetone) and record the result.

#### 3. 2,4-DNPH

Add 2 cm<sup>3</sup> of 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent (i.e., sometimes called, *Brady's reagent*) to a boiling tube. Add 5 drops of benzenecarbaldehyde (benzaldehyde) and swirl the mixture. **Take care with the 2,4-DNPH reagent since it is readily absorbed through the skin and is toxic; wash it off immediately with soap and water if you accidentally get it on your skin.** Describe the result of your test. Repeat using a ketone such as propanone and record the result.

### ORGANIC ACIDS

#### 1. Solubility

Introduce 10 cm<sup>3</sup> of water into a small beaker. Add 5 drops of glacial acetic acid (ethanoic acid); swirl gently to mix. Test this solution with litmus and pH paper (range 1-14). Record the pH value. Note that the acetic acid is very soluble in water. It also partially dissociates in water. Test the solubility of the aromatic acid, benzoic acid, in water. Is it very soluble, fairly soluble or slightly soluble? Test the aqueous solution with pH paper. Is the acid more soluble in warm water?

Introduce 2 cm<sup>3</sup> of toluene into a test-tube. Add 3-4 drops of acetic acid. Does it appear to be soluble? Repeat the test using benzoic acid. Is it soluble to any extent? (NOTE: Pour the toluene solutions away in the solvent residue bottle which you will find in the fume-hood).

Organic acids are polar molecules and are generally soluble in polar solvents such as water and alcohols.

#### 2. Alkali

Introduce 2 cm<sup>3</sup> of dilute (2M) sodium hydroxide into a test-tube. From a spatula add a small amount of benzoic acid. Swirl the mixture. How soluble is the acid in the alkali (very, fairly, sparingly)? Carefully add dilute (2M) hydrochloric acid to the test-tube until acid to litmus. Cool the tube in iced water. Record and explain the changes.

### 3. Sodium Carbonate

Introduce 2 cm<sup>3</sup> of sodium carbonate solution (10%) into a boiling tube. Add acetic acid dropwise. Note if any gas is evolved. If so, identify the gas.

Repeat the test using benzoic acid instead of acetic acid. What is the main difference?

### 4. Esterification

Introduce 2 cm<sup>3</sup> of pentan-1-ol (amyl alcohol) into a boiling tube. Add 2 cm<sup>3</sup> of acetic acid and then 2 drops of concentrated sulphuric acid (**CARE: highly corrosive**). Swirl the mixture gently. Warm the tube in hot water (use a water-bath) for about 5 minutes. Very carefully pour the contents of the tube into about 50 cm<sup>3</sup> of dilute sodium carbonate solution (10%) contained in a 250 cm<sup>3</sup> beaker. Note any smell issuing from the beaker. Describe the smell. What class of compound is this due to?

Repeat the test using ethanol and then propan-1-ol instead of amyl alcohol. Describe the results.

### 5. Iron(III) Chloride

Introduce 4 cm<sup>3</sup> of iron(III) chloride solution into a test-tube. Add 2 or 3 drops of dilute (2M) ammonia solution and filter, collecting the filtrate in a boiling tube. Place 1-2 cm<sup>3</sup> of acetic acid in another boiling tube and add dilute ammonia until alkaline to litmus. Pour the contents of the tube into a small beaker and gently boil the mixture until excess ammonia has been evolved. The volume can be maintained with distilled water. Cool the contents of the beaker and pour into the iron(III) chloride solution (which is contained in the first boiling tube). The purpose of adding ammonia solution to both iron chloride and the acid is to ensure that both reagents are approximately neutral before they are mixed. What do you observe on mixing the reagents? Repeat the test using benzoic acid instead of acetic acid. Describe the result.

### 6. Phosphorus Pentachloride

Introduce 2 cm<sup>3</sup> of glacial acetic acid into a boiling tube. With the tube in a fume-hood, add a small quantity (from a spatula) of phosphorus pentachloride. Note the vigorous reaction and the evolution of a gas. The gas is hydrogen chloride and may be tested for with damp litmus and ammonia fumes. What are the results of these tests?

The organic product is an acid chloride, acetyl chloride (ethanoyl chloride).

Other organic acids react similarly. Acid chlorides may be converted to amides (RCONHR' where R= alkyl and R' = alkyl or hydrogen) by reaction with ammonia or a primary amine.

## AMINES

### 1. Odour & Basicity

Pour 1 cm<sup>3</sup> of aqueous methanamine (methylamine) solution into a boiling tube. **CAUTIOUSLY** waft the vapour towards you and detect the characteristic odour. What does it remind you of? Using indicator paper measure the pH of the solution. Record and explain the result.

### 2. Solubility.

Introduce 2 cm<sup>3</sup> of each of the following into separate test-tubes: water, dilute (2M) hydrochloric acid, dilute (2M) sodium hydroxide (**CARE: acids and alkalis are corrosive to the skin**)

Add, dropwise, to each tube 1 cm<sup>3</sup> of benzenamine (aniline). Gently swirl the tubes, during the addition, and determine whether benzenamine is soluble in each reagent. Explain any differences.

### 3. Diazonium Compounds

**When you have completed the following tests discard all solutions down the fume cupboard sink, washing away with plenty of water** (diazonium compounds should not be allowed to dry out since many are unstable and potentially explosive)

Make a dilute solution of sodium nitrite (e.g., 2 spatulas of the salt in 3 cm<sup>3</sup> of distilled water) in a boiling tube. Cool the solution in *iced* water. Add 1 cm<sup>3</sup> of *ice cold* dilute hydrochloric acid. You should now have a dilute solution of **nitrous acid**, which is very pale blue. Divide the solution into two equal parts (using a second test-tube). To one part add, dropwise, *ice cold* methanamine solution. Notice and record what happens. To the other part add 2-3 drops of benzenamine and swirl; then add 2-3 drops of *ice-cold*, alkaline, 2-naphthol solution. Record and explain the result.

### 4. Amides

Amines react readily with acid chlorides forming amides. Introduce 0.5 cm<sup>3</sup> of benzenamine (aniline) into a boiling tube. Add approximately 10 cm<sup>3</sup> of 2M sodium hydroxide solution followed by 0.5 cm<sup>3</sup> of benzenecarbonyl chloride (benzoyl chloride). (**CARE: sodium hydroxide is caustic and benzoyl chloride is lachrymatory, i.e., makes your eyes water. Take care not to get either substance on your skin.**) Having introduced the reagents into the tube, cork the tube (use a well fitting cork - one which does not leak; do not use a rubber bung) and shake thoroughly for about 10-15 minutes, **releasing the pressure at frequent intervals by momentarily removing the cork from the tube.**

When reaction is complete and excess acid chloride has been hydrolysed, you should have granules of crude product (i.e., amide). Filter, wash the solid residue with plenty of water. Dry the purified material thoroughly (in an externally vented oven at 90°C) and take its melting point. Compare with and state the literature value (you may find your mp is low compared with the literature value. Better agreement can be obtained by recrystallising your crude product). State your % yield.

### A suggestion for a mini project:

#### Nitration of salicylic acid, acetylsalicylic (aspirin) or even benzoic acid.

General procedure:

Weigh out a known quantity of starting material (about 1 g) into a small beaker (100 ml). Add 60 ml of dil. nitric acid (ie, 15% : 20 ml of concentrated + 80 ml of distilled water). Boil in a fume cupboard for about 10 minutes.

Pour the reaction mixture into 80 ml of distilled water. Stir and cool in ice-water. Filter off the white or yellowish solid. Recrystallise from IMS/water (1:1). Dry.

Record mass of recrystallised material. Store in labelled vial.

Measure its melting point. Obtain infra red spectrum (if possible!).

If you started with salicylic acid your product should melt at 224-226°C.

If you started with aspirin your product should melt at 225°C.

If you started with benzoic acid your product should melt at 140°C.

Try and identify your products. Write possible structural formulae.

If you can obtain ir spectra of your products compare them with standard spectra from the literature.

Note that dilute nitric acid (15%) is being used (& **not** concentrated nitric + sulphuric). The electrophile on this occasion is the nitrosonium ion  $\text{NO}^+$  generated from reaction between nitric(III) acid and nitric(V) acid.

# Practical Sixteen

## Potentiometric Titrations

### Safety:

Wear safety spectacles at all times in the laboratory.

Acids and alkalis are caustic avoid skin contact. In the event of accidental contact wash the affected area thoroughly with plenty of cold, clean, water.

Take care when assembling and using glassware particularly when using glass pipettes. When applying pipette fillers hold the stem of the pipette near the end to which the filler is fitted. Ask for advice if in doubt. When introducing alkali into the burette use a plastic funnel and make sure the funnel is below eye level to avoid splashing alkali into your eye. Do **not** stand on a chair or stool to reach the top of the burette.

Take care when connecting electrical equipment; do not connect to the mains before assembling your apparatus. Similarly, disconnect electrical equipment from the main before dismantling your apparatus. Take care with electrodes, they are fragile.

### PROCEDURE

Set up the equipment for potentiometric titration (see diagram below or refer to notes/textbook). After rinsing the electrode assembly with distilled water, check the pH meter by dipping the electrodes into standard buffer solution. Adjust the meter so that its pH reading agrees with the stated pH of the buffer solution (use pH 4 & 7 buffers).

Place 25.00 cm<sup>3</sup> of the **unknown acid** (1 below) in a 250 cm<sup>3</sup> beaker. Dip the electrode into the solution, adding distilled water until covered sufficiently. Take a pH reading.

Run into the beaker 4.0 cm<sup>3</sup> of standard 0.1M (2 below) sodium hydroxide solution from a burette and, after stirring well, take another pH reading.

Take pH readings after each 4.0 cm<sup>3</sup> addition of alkali until about 5 cm<sup>3</sup> from the end-point, when 1.0 cm<sup>3</sup> additions should be made, and finally 0.2 cm<sup>3</sup> additions when close to the end-point. Make further additions until about 10 cm<sup>3</sup> beyond the end-point.

Plot a graph of pH against volume of sodium hydroxide added, note the pH at the end-point. Calculate the molarity of the acid.

When not in use the electrode must be rinsed with distilled water and stored in a boiling tube containing distilled water.

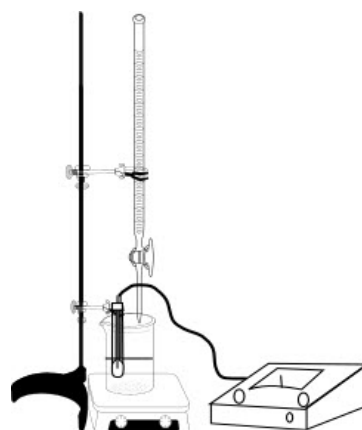
If required, repeat the exercise using other unknown acid(s). Calculate the molarities of these acids.

You can also find the  $K_a$  of a weak acid (see theory pages). You could also titrate vinegar against dil. NaOH and find the concentration of ethanoic acid.

1. Details of the acid will be provided by the lecturer
2. The lecturer or technician will provide the precise molarity

### Questions

1. Sketch and label calomel and glass electrodes or a glass combination electrode.
2. What are the advantages of potentiometric titrations over ordinary titrations using indicators?
3. Describe and illustrate a procedure for accurately deducing the end-point from the results of a potentiometric titration (other than by plotting the simple pH titration curve).
4. Sketch the general shapes of pH titration curves for, (i) strong acid titrated against strong base, (ii) strong acid titrated against weak base (e.g., ammonia), (iii) weak acid (e.g., ethanoic acid) against strong base. What are the main differences?
5. What type of acids are the unknown acids?



# Practical Seventeen

## Redox Reactions & Electrochemical Cells

### Experiment:

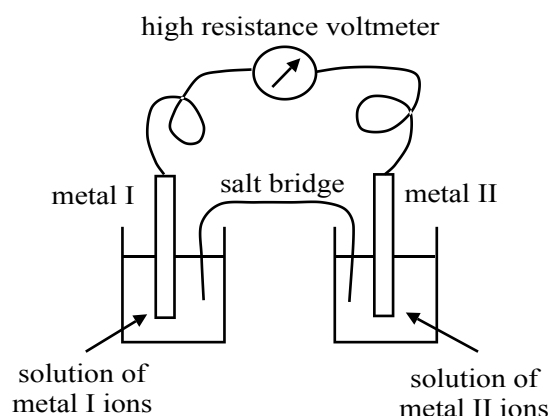
#### Measuring Cell EMF's

This experiment involves the construction of **three** electrochemical cells to measure their EMF's and determine the polarity of the electrode half-cells.

**Safety: Wear safety spectacles. Avoid skin contact with all chemicals. In the event of accidental contact wash the affected area immediately with copious amounts of cold, clean, water.**

Make sure the metal strips are clean. Use emery paper as necessary.

By following the photograph and diagram, shown below, assemble the two beakers representing the two half-cells (choose a pair from the table below).



Half-cells		
Cell	Metal II	Metal I
1	$\text{Zn}^{2+}(\text{aq}) 1\text{M} + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	$\text{Cu}^{2+}(\text{aq}) 1\text{M} + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$
2	$\text{Ag}^+(\text{aq}) 0.1\text{M} + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	$\text{Cu}^{2+}(\text{aq}) 1\text{M} + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$
3	$\text{Ag}^+(\text{aq}) 0.1\text{M} + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	$\text{Zn}^{2+}(\text{aq}) 1\text{M} + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$

The salt bridge allows electrical conduction between the two half cells without the solutions mixing.

Prepare this salt bridge by soaking a thin strip of filter paper in the potassium nitrate solution. Allow surplus solution to drain from it and then connect the beakers as shown using this salt bridge.

Finally connect the two metal electrodes to the high resistance voltmeter as shown. The connections must be such that a positive EMF value for the cell is obtained.

Note the polarity of the electrodes, measure the EMF of each cell and complete the table. Record the temperature of the cell solutions.

Cell	Positive Electrode	Negative Electrode	EMF/V
1			
2			
3			

### Questions:

- For each cell in turn write the half equation representing the reaction at each electrode. Then combine these to produce the overall cell reaction.
- Compare your cell EMF with the values calculated from the standard electrode potentials given below. Comment on any differences.

Electrode	Half-Reaction	Standard Electrode Potential/ V
$\text{Zn}^{2+}(\text{aq})/\text{Zn}(\text{s})$	$\text{Zn}^{2+}(\text{aq})\ 1\text{M} + 2\text{e}^{-} \rightleftharpoons \text{Zn}(\text{s})$	<b>-0.76</b>
$2\text{H}^{+}(\text{aq})/\text{H}_2(\text{g})$	$2\text{H}^{+}(\text{aq})\ 1\text{M} + 2\text{e}^{-} \rightleftharpoons \text{H}_2(\text{g})$	<b>0.00</b>
$\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$	$\text{Cu}^{2+}(\text{aq})\ 1\text{M} + 2\text{e}^{-} \rightleftharpoons \text{Cu}(\text{s})$	<b>+0.34</b>
$\text{Ag}^{+}(\text{aq})/\text{Ag}(\text{s})$	$\text{Ag}^{+}(\text{aq})\ 1\text{M} + \text{e}^{-} \rightleftharpoons \text{Ag}(\text{s})$	<b>+0.80</b>

These values refer to the cell:



# Practical Eighteen

## Electrolysis

Electrolysis is the decomposition of a compound in solution or in the molten state by passing an electric current through it.

Electrolysis is readily illustrated in the laboratory. The following experiments are examples.

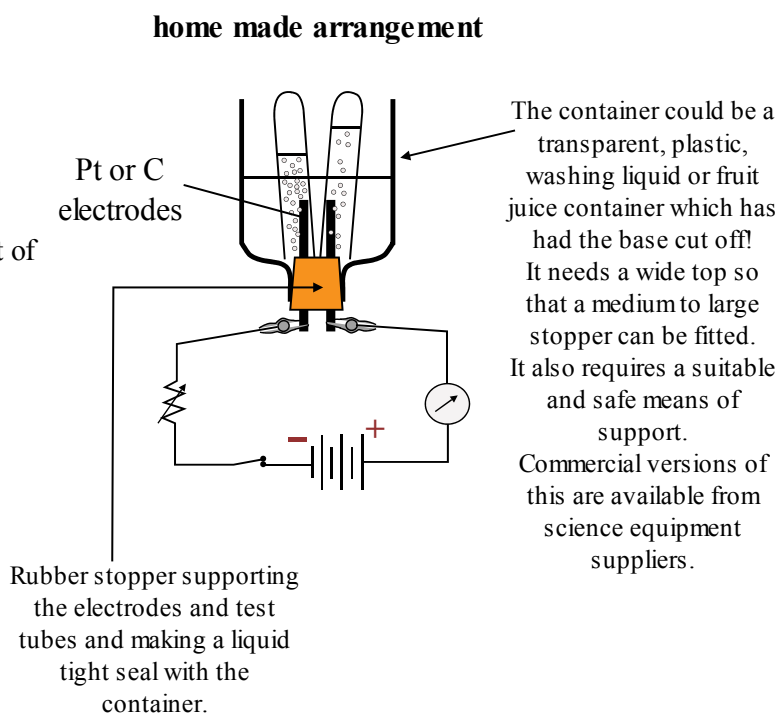
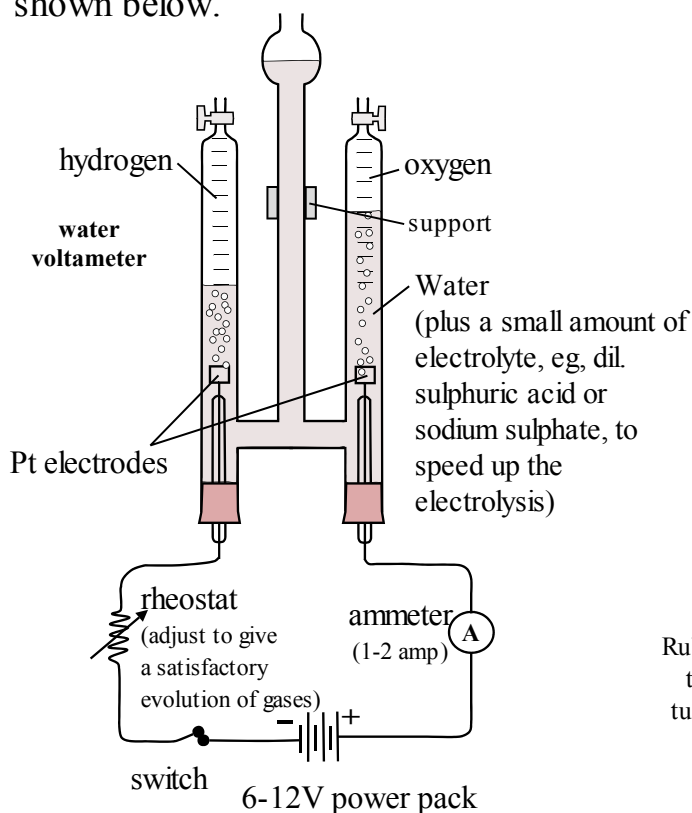
### Safety note:

As with all experimental work, make detailed plans and carry out a risk assessment. Check the potential hazards of all chemicals and make sure all equipment is safe to use. It may be necessary to perform experiments under a fume-hood if toxic gases or fumes are involved. Check your procedure and equipment with the teacher or qualified laboratory technician before starting.

### The Electrolysis of Water.

This can be achieved on a small scale using a plastic bottle to contain the water (acidified with a little dilute sulphuric acid), test-tubes (to collect the gases) and platinum or carbon electrodes.

However, it is most conveniently illustrated in a water voltameter (also, *Hoffmann voltameter*) as shown below.

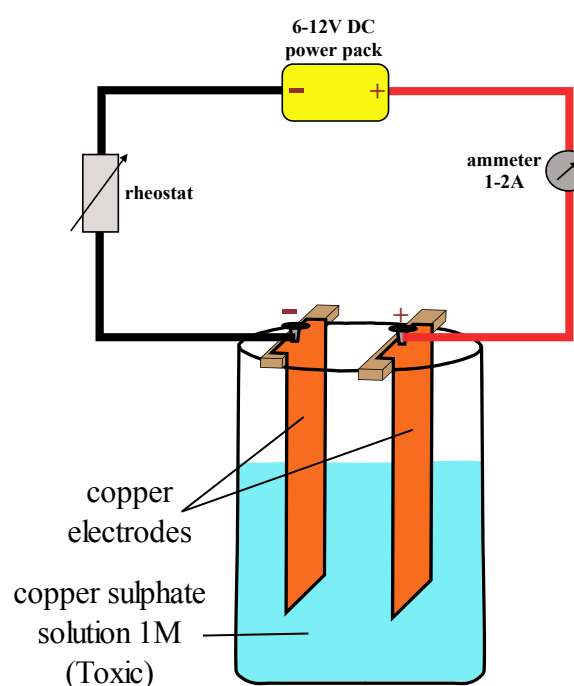




Having electrolysed water, note the proportions of gases collected. Carefully test each gas. Hydrogen *pops* when ignited in air. Oxygen relights a glowing splint. Write equations for the reactions occurring at the electrodes.

## Electrolysis of Copper sulphate solution:

Set up the following cell:



1. Obtain a pair of copper electrodes. These can be bought from an educational chemical supplier or made by cutting from a roll of sheet copper (*this is a job for the laboratory technician; take care to avoid sharp metal edges!*). The electrodes can be 1.5 x 8 cm.

2. Make sure the copper electrodes are clean before starting the experiment. The metal can be cleaned by rubbing with emery paper or steel wool (care!) and rinsing first with water (or dilute ammonia solution) and then with propanone (acetone). The latter is miscible with water, volatile and serves to dry off the electrodes. **Note, however, that propanone is highly flammable and must be kept well away from naked flames.**

3. Mark the electrodes to record which is the cathode and which the anode. Weigh the electrodes. Suspend the electrodes from strips of wood (or a wood frame) laid across the top of a glass beaker and secured with pins or crocodile clips connected to the electric leads. Arrange it so that 4 to 5 cm of the electrodes are immersed in the copper sulphate solution.
4. Switch on the supply and pass a known current (eg, 1A) for a measured time interval (eg, 25 minutes). Switch off the supply and carefully rinse the electrodes in water and then propanone. Take care not to accidentally remove any deposit. When dry, weigh the electrodes. You should find that the cathode has increased in mass and the anode has decreased in mass. Furthermore the increase in mass should equal the decrease in mass. Within experimental error, do your results confirm this?
5. Repeat the experiment but this time increase the quantity of electricity passed (ie, longer time and/or higher current). Record and comment on, the change in masses of the electrodes.
6. Show that your results support Faradays Laws (see next page).
7. As an extension to the exercise you could investigate the effect of temperature on the course of the electrolysis by warming or cooling the copper sulphate solution just prior to electrolysis. You would need to record the temperature and keep the other variables constant.

[Michael Faraday](#) (1791 - 1867) electrolysed many substances and formulated two important laws. These may be summarised as follows:

### **The First Law:**

**Mass of substance (deposited or liberated)  $\propto$  Quantity of electricity passed**

or,

$$m = z.I.t$$

where,  $m$  = mass deposited or liberated

$I$  = current in amps

$t$  = time in seconds

$z$  = a constant (the *electrochemical equivalent*)

and ( $I \times t$ ) = amount of electricity in coulombs

The constant known as the electrochemical equivalent is the mass (in grams) of substance deposited or liberated by the passage of 1 coulomb of electricity. It is a very small quantity.

eg, 0.00118 for silver, 0.00001045 for hydrogen and 0.000329 for copper.

### **The Second Law:**

**The quantity of electricity required to deposit 1 mole of a substance in electrolysis is always an integral number (ie, a whole number) of faraday's (ie, 1, 2 or 3).**

A faraday is the charge on 1 mole of electrons or 96 480 coulombs (the *Faraday constant*).

To deposit 1 mole of copper from a solution of copper(II) sulphate would require 2 faradays of charge, ie, 2 x 96 480 C.

# Practical Nineteen

## Qualitative Organic Analysis:

It is possible to identify a pure, unknown, organic substance by applying simple chemical tests, making derivatives and obtaining mpts and/or bpts.

Mpts and bpts are compared with data available in the literature (your teacher will refer you to suitable textbooks, catalogues and internet sites).

Details of a scheme for carrying out this type of analysis is given in the following pages.

This scheme is just one example of a possible *modus operandi*; your teacher may have an alternative scheme or may be able to recommend improvements to the one given.

The results of your chemical analyses can be confirmed if you have access to instrumental methods of analysis (eg, ms, ir, uv, pmr).

The whole process provides an excellent way of learning organic chemistry and acquiring important laboratory skills.

As with all practical work, you will get better at it the more you practice!

## Qualitative Organic Analysis

The object here is to identify a simple organic substance. Your teacher will provide you with a few grams of a pure organic compound. It may be a liquid or a solid and it will have an identifying code.

Tabulate your results (ie, obtain an A4 notebook and divide a few pages into three columns, headed, TEST, OBSERVATION, INFERENCE). It is important that you record all your analyses in a careful and systematic way.

### 1. Preliminary Analyses:

#### (a) Sodium Fusion (Lassaigne test).

This is to establish the presence of nitrogen, sulphur, phosphorus and halogens.

**(CARE: It is recommended that the fusion is performed in a fume cupboard.**

**Your teacher will demonstrate the procedure to you.**

**Wear safety spectacles throughout)**

#### (i) Solids.

Add the organic substance (ca 50 mg) to a small piece of sodium (about a 2 mm cube or the same volume as the compacted organic substance) in the bottom of an *ignition tube* (these are miniature test tubes (about 5 x 40 mm) made of soda glass). Try and ensure that some of the substance is both above and below the sodium in the tube. Heat the mixture gently at first so as to melt the sodium and allow it to start reacting with the unknown substance. Move the tube in and out of the bunsen flame so as to control the amount of heat being delivered to the reaction mixture and to ensure that the mixture stays in the tube during the heating process. This reaction may be vigorous so it is advisable to hold a metal gauze over the mouth of the tube to protect yourself (and your neighbours if you happen to be working in the open laboratory). At this stage, test for **phosphorus** by holding a strip of filter paper soaked in silver nitrate to the mouth of the tube. If phosphorus is present the paper will turn black immediately.

Continue heating the mixture allowing any distillate to run back onto the sodium. When the contents of the tube begin to char, heat the tube to dull redness for about 30 seconds.

Whilst the tube is still hot drop it into about 5 cm<sup>3</sup> of distilled water contained in a clean evaporating basin (or boiling tube supported in a test tube rack), placing a metal gauze over the basin (or tube) as you do so (this is just to contain any spitting as the hot tube makes contact with the water). The ignition tube will shatter and any remaining sodium will react with the water. When the reaction is complete, heat the contents of the basin (or tube) to boiling and filter off the broken glass, etc. Put the filter paper containing the glass in the glass bin. The filtrate should be clear, colourless or nearly colourless, and alkaline. If the filtrate is darkly coloured repeat the sodium fusion.

**Note:** If you find that the sample volatilises from the ignition tube before it has a chance to react with the sodium, try covering the sample and sodium with a layer of anhydrous sodium carbonate before heating the mixture. This will help retain the sample long enough for it to react with the sodium.

#### (ii) Liquids.

Heat a very small piece of sodium (see note above) in a clean ignition tube until it begins to melt. Then, using a glass teat pipette, let two small drops of the liquid sample fall onto the sodium. Allow the reaction to occur holding a metal gauze over the mouth of the tube (just in case there is any spitting). Warm the tube again and add two more drops of liquid sample. Whilst holding the metal gauze over the mouth of the tube heat the tube to redness. From here on, complete the procedure as for a solid sample.

continued:-

### (iii) Filtrate.

Divide the filtrate into *four* portions and apply the following tests:

**Test for Nitrogen:** Add a portion of the filtrate to a small volume of freshly prepared iron(II) sulphate solution in a boiling tube. Heat the mixture to boiling and boil for about 30 seconds (**CARE!**). Cool and add dilute sulphuric acid until the mixture becomes acid. A blue colour or blue precipitate indicates nitrogen. If the solution is colourless or yellow, nitrogen is absent. If the solution is green allow it to stand. A blue colour may develop. If it does not, the result is doubtful and the sodium fusion should be repeated.

The blue colour (or precipitate) is sometimes more apparent when the solution is filtered and the dry filter paper examined. Blue material often shows clearly against the white background of the paper.

**Test for Sulphur:** To another portion of the filtrate add a small volume of 1% freshly prepared sodium nitroprusside solution. A rich purple colour indicates sulphur. The test is sensitive. Only strong colours are significant.

**Test for Halogens:** If you find that nitrogen or sulphur *are* present acidify another portion of the filtrate with dilute nitric acid and boil gently for two minutes. This will remove cyanide or sulphide ion so that they do not interfere with the halide test.

Add a little more dilute nitric acid followed by dilute silver nitrate solution. A cream or white precipitate indicates halogen.

Test the precipitate for solubility in dilute ammonia solution. White silver chloride is soluble, cream silver bromide slightly soluble and yellow silver iodide insoluble.

Also, you can try acidifying a portion of the original filtrate with dilute hydrochloric acid, adding 0.5 cm<sup>3</sup> of dichloromethane and a few drops of sodium chlorate(I) (hypochlorite) solution. After mixing, a yellow or brown organic layer indicates bromine whereas a violet layer indicates iodine.

---

### (b ) Physical Characteristics.

Record the colour and physical state of the unknown substance. Test its solubility in water, industrial methylated spirit (IMS: this is 95% ethanol) and hexane. This will indicate its polarity.

Shake a small quantity of the unknown with water and estimate the pH of the aqueous solution (using universal indicator paper).

Most organic compounds are colourless but a few do have colour. Some unsaturated compounds are pale yellow as are some nitro compounds.

If you find that the aqueous solution of the compound is acidic it could be a carboxylic acid, sulphonic acid, phenol or amine salt. If the solution is alkaline the compounds could be an amine or salt of a weak acid.

### (c) Action of Heat.

Burn a small quantity (the equivalent of 2 or 3 drops) on a crucible lid. Perform this test in a fume cupboard.

Sooty flame: high carbon content, ie, aromatic or unsaturated.

Clean flame: low carbon content, ie, saturated aliphatic.

Non-flammable: this is rare but it may indicate high halogen content.

After heating strongly for some time, is there a residue? If so, this is possibly due to a metallic salt. Identify the metal by inorganic analysis.

continued:-

#### (d) Halide and Sulphate.

If the unknown is soluble in water try tests for,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$  &  $\text{SO}_4^{2-}$ .

Halides: Dissolve a little of the substance in distilled water, acidify with dilute nitric acid and add dilute silver nitrate solution (**CARE**: both of these solutions are caustic). A precipitate indicates halide.

Sulphate: Dissolve a little of the substance in water, acidify with dilute hydrochloric acid and add dilute barium chloride solution (**CARE**: the acid is corrosive and the barium chloride toxic). A white precipitate indicates sulphate.

#### (e) Action of 2M Sodium hydroxide solution (**CARE**: this solution is caustic).

Examine the substance in cold sodium hydroxide solution and then in *warm* solution (DO NOT BOIL).

(i) If it is soluble in the cold it is an acidic substance (carboxylic acid or phenol).

(ii) If ammonia is evolved in the cold it is an ammonium salt.

(iii) If ammonia is evolved on heating it is a simple amide.

(iv) If a resinous material is formed (brownish jelly-like) it could be an aldehyde (not methanal or benzenecarbaldehyde).

(v) If you observe a fishy smelling alkaline vapour it could be a simple amine salt.

#### (f) Action of Potassium permanganate solution (about 0.005 M).

Add a very small quantity of the unknown to a very dilute solution of permanganate containing one drop of dilute sodium hydroxide.

Loss of the purple colour indicates a reducing agent or unsaturated compound.

#### (g) Action of Bromine.

Take a small sample of the unknown substance and add it to 2 cm<sup>3</sup> of bromine water. Mix thoroughly. An unsaturated substance will discharge the colour of bromine (ie, reddish-brown to colourless). (Note: The bromine solution needs to be dilute so that any colour change can readily be observed.)

(The test with bromine works better if the bromine is dissolved in tetrachloromethane to give a 0.1% solution. However, tetrachloromethane is one of those solvents which it is recommended should not be used in schools and colleges because of its toxic nature.)

#### (h) Action of 2,4-Dinitrophenylhydrazine (2,4-DNP).

Add one drop (or an equivalent amount if solid) of the unknown organic substance to 0.5 cm<sup>3</sup> of *Brady's reagent*. An immediate orange-yellow precipitate indicates that aldehyde or ketone is present.

A precipitate after warming and cooling may indicate an unreactive carbonyl compound or a reducing sugar.

**(Brady's reagent:** 2,4-DNP dissolved in methanol acidified with a little concentrated sulphuric acid - this is normally a bench reagent and would be made up by the laboratory technician. *It is corrosive, toxic and flammable*).

#### (i) Action of 10% Sodium Carbonate solution.

Add a small quantity of the unknown organic substance to about 2 cm<sup>3</sup> of sodium carbonate solution. If it is soluble with effervescence a carboxylic acid is indicated. This would need to be confirmed later by applying further tests (such as esterification).

Reaction of the carboxylic acid with aqueous carbonate is sometimes slow and bubbles of carbon dioxide gas accumulate slowly in the unreacted solid.

### (j) Melting point/Boiling point.

Measure the melting point of an organic solid. Measure the boiling point of an organic liquid (the small scale *Siwoloboff method* is usually suitable-- ask your teacher for details).

When you have completed the *preliminary analyses* you should have enough information about the unknown substance to be able to suggest which **functional group** is present (In more complex cases the substance may contain more than one functional group). You may also have strong suspicions as to the identity of the substance but you will need to confirm your suspicions with firm evidence.

The following table may help you to classify your unknown substance and give you a lead as to what to do next.

Elements present	Classifications
CH(O) only	Alcohol, aldehyde, ketone, carboxylic acid, ester, acid anhydride
CH(O)Halogens	Halogenoalkane, acid halide
CH(O)Nitrogen	Ammonium salt, amide, amine
CH(O)Nitrogen+Halogen	Amine salt
CH(O)Sulphur	Hydrogensulphite compound of aldehyde and ketone, sulphonic acid
CH(O)Nitrogen+Sulphur	Amine sulphate, sulphonamide
CH(O)Phosphorus	Organophosphorus compound (eg, ester & phosphorus alkyl)

If, for example, your preliminary tests are negative for the elements phosphorus, nitrogen, sulphur and halogens you can confine your subsequent analyses to the first classification in the table above. If your substance burns with a clean flame it is probably aliphatic and saturated. Furthermore, if it gives an orange precipitate with 2,4-DNP and all other tests are negative, it is an aldehyde or a ketone. You can then concentrate your attention on finding out which aldehyde or ketone you have been given!

## 2. Confirmatory Analyses.

### (a ) Tests to confirm and distinguish aldehydes and ketones.

**(i) Tollens' reagent:** Add one drop of dilute sodium hydroxide to 5 cm<sup>3</sup> of dilute silver nitrate solution in a test tube. Add dilute ammonia solution, *dropwise*, so as to just dissolve the grey precipitate. This mixture is known as Tollens reagent after the German chemist, Bernhard Tollens (1841-1918). Add a small quantity of the unknown to the Tollens reagent and mix. An immediate black precipitate or silver mirror indicates an aliphatic aldehyde. Slow formation of silver indicates an aromatic aldehyde or reducing sugar (sometimes it is necessary to gently warm (**not** boil!) the reaction mixture in the latter case).

Wash the test reagents away down the fume cupboard sink when you have completed the test. Tollens reagent is not a *bench* reagent; it must be made and used fresh since it is **unstable**.

Tollens reagent can be used to distinguish aldehydes and ketones since the latter do not react.

**(ii) Schiff's reagent:** An immediate red colour when the unknown is added to Schiff's reagent indicates an aldehyde. A slight reddish colour indicates a reactive ketone or unreactive aldehyde. Schiff's reagent is an aqueous solution of pararosaniline and sulphuric(IV) acid. It is colourless when freshly made. The reagent is named after the German chemist, Hugo Schiff (1834-1915).

**(iii) Fehling's reagent:** Mix equal volumes of Fehling's A & B. Add 50 mg of the unknown to 2 cm<sup>3</sup> of the mixed Fehling's reagent in a boiling tube. Leave the tube in a beaker of gently boiling water for 2 minutes. A yellow, green, orange or red precipitate indicates aldehyde. Aromatic aldehydes react slowly if at all. Ketones, except for  $\alpha$ -hydroxyketones, do not react. Fehling's A is copper sulphate solution. Fehling's B is a mixture of sodium hydroxide and potassium sodium tartrate solution. A & B are mixed when required. The reagent is named after the German chemist Herman von Fehling (1812-1885).

**Conclusion:** If the unknown organic substance gives a positive with 2,4-DNP it is a carbonyl compound; an aldehyde or a ketone. If the unknown then reacts negatively with the above reagents ( ie, (i), (ii), (iii) ) it is a ketone. If it reacts positively with the above reagents it is an aldehyde.

### **(b) Test for Carboxylic Acids.**

**Esterification:** Warm a small amount of the unknown organic compound, in a small beaker or boiling tube, with twice its volume of industrial methylated spirit (IMS) and about a half its volume of concentrated sulphuric acid for 1-2 minutes. (**CARE:** this acid is highly corrosive. Mix it in carefully with a glass rod before warming the mixture).

**General safety note:** mixtures containing organic solvents must **not** be heated directly using a bunsen flame. In this test, the esterification mixture can be heated indirectly on an electrically heated water bath in the fume cupboard.

After warming, carefully pour the reaction mixture into a large beaker containing excess water (eg, 100 cm<sup>3</sup>). Cautiously smell the vapours from the beaker by wafting the vapours towards you. A fruity smell indicates ester and a carboxylic acid of low molecular mass.

**Note:** The ethyl esters of high molecular mass are almost odourless. Also, esterification can be used to test for alcohols by using ethanoic acid (glacial acetic acid) in place of IMS.

### **(c) Test for Phenols.**

**Phthalein reactions:** Warm together in a dry test tube 50 mg of the unknown, twice its volume of phthalic anhydride and 1 drop of concentrated sulphuric acid (**CARE!**) for 1-2 mins. Do not over-heat. Cool, add a few drops of methanol and an excess of aqueous dilute sodium hydroxide. Red, green, blue or purple colour indicates a phenol, however, some phenols do not react.

### **(d) Test for Hydroxy group.**

**Phosphorus pentachloride:** In a dry test tube add a little phosphorus pentachloride to a dry sample of the unknown. In the case of a solid unknown it may be necessary to mix the reactants in a small mortar - in a fume cupboard. Evolution of hydrogen chloride indicates hydroxyl group (-OH) as in an alcohol, phenol or acid - although phenols do not react at all readily with phosphorus pentachloride.

**Note:** reactants and apparatus must be DRY for the results to be meaningful.

### **(e) Test for Alcohol.**

**Ceric ammonium nitrate:** Agitate a solution or suspension of the unknown in water with 1 cm<sup>3</sup> of 10% ceric(IV) ammonium nitrate in dilute nitric acid.

(i) reddish brown colour - OH group present in an alcohol.

(ii) red colour rapidly fading - polyhydric or easily oxidised alcohol.



**(f) Test for  $\text{CH}_3\text{CHOH}$ - &/or  $\text{CH}_3\text{CO}$ - group.**

**Iodoform test:** To 5 drops of the unknown add  $1\text{ cm}^3$  of 10% potassium iodide solution, warm and then add up to  $5\text{ cm}^3$  of sodium chlorate(I) (hypochlorite) solution. Look for a yellow precipitate of iodoform.

**(g) Test for Ester.**

To a boiling tube add  $5\text{ cm}^3$  of 10% potassium hydroxide (**CARE:** caustic), about 0.2g of hydroxylamine hydrochloride and a small amount of the unknown (eg, a few drops). Gently, with swirling, heat the mixture to near boiling for 1-2 minutes (**CARE**). Cool the mixture and acidify with dilute hydrochloric acid. Cool again and add a few drops of iron(III) chloride solution. A deep red colour indicates the presence of ester.

The ester reacts with hydroxylamine to give a hydroxamic acid ( $\text{RCONHOH}$ ) which forms a red complex with iron(III).

(Note: Acid chlorides and anhydrides also give a positive test with this reagent)

**(h) Test for NH group in amides and amines.**

**Nitric(III) acid (nitrous acid):** To  $1\text{ cm}^3$  of an ice *chilled* concentrated sodium nitrate(III) (ie. nitrite) solution add  $1\text{ cm}^3$  of dilute (4M) ethanoic acid. Allow the evolution of gas to subside then drop in a small amount of the unknown substance. A brisk evolution of nitrogen gas indicates a simple amide or primary amine.

**(i) Test for nitro group.**

**Titanium(III) chloride:** In a boiling tube, dissolve 100 mg of the unknown in  $5\text{ cm}^3$  propanone (**CARE:** highly flammable). Add  $5\text{ cm}^3$  of titanium(III) chloride solution. Warm the mixture in a water bath. Loss of colour within 2 minutes indicates a nitro compound.

(Note: this test is also given by azo, azoxy, hydrazo, nitroso, nitrites, hydroxylamines & quinones.)

**(j) Test for Amino-acids.**

**Ninhydrin reagent:** Add a little of the unknown to  $3\text{ cm}^3$  of distilled water in a test tube. Add a few drops of 0.25% aqueous solution of ninhydrin (**CARE:**poisonous). A blue or violet colour indicates amino-acid.

Amino-acids often give positive results for  $-\text{NH}_2$  and  $-\text{COOH}$  groups.

---

Having established which functional group(s) are present in the unknown, the final stage in the analysis involves preparing a couple of derivatives of the unknown. Ideally, these derivatives should be crystalline solids so that their melting points can be measured accurately. The melting points of these derivatives along with the physical and chemical characteristics of the unknown are used to confirm the identity of the unknown.

A selection of possible derivative preparations are given in the next section.

## Derivative Preparations.

### 1. Carboxylic Acids:

#### Amide derivatives:

##### (a) Convert the acid to the acid chloride.

Introduce 1 g of the acid into a 100 cm<sup>3</sup> conical flask. With the flask in the fume cupboard, add 1 cm<sup>3</sup> of thionyl chloride (SOCl<sub>2</sub>, **CARE**: corrosive, fuming liquid) and 5 drops of dimethylformamide (DMF). Attach a calcium chloride drying tube and heat the flask on a water bath, in the fume cupboard, at 50-60°C for 15 to 20 minutes.

##### (b) Convert the acid chloride to either a *simple amide* or a *substituted amide*.

(i) Simple amide: Add the acid chloride from the above preparation, dropwise, with vigorous stirring to 15 cm<sup>3</sup> of ice-cold 0.88 ammonia solution (**CARE**: pungent fumes, vigorous reaction .... DO THIS IN THE FUME CUPBOARD). Filter, to isolate the amide. Recrystallise to constant melting point from water, water-alcohol or alcohol.

(ii) Substituted amide: Add the acid chloride from (a) gradually with stirring, to 2 cm<sup>3</sup> of benzenamine (aniline) in a 250 cm<sup>3</sup> beaker (again take **care**: fumes are evolved and reaction is vigorous). Add 15 cm<sup>3</sup> of water and 2 cm<sup>3</sup> of concentrated hydrochloric acid. Filter and recrystallise to constant melting point.

### 2. Phenols:

Nitrobenzoate: In a small, clean, mortar dissolve 0.4 g of the phenol in 10 cm<sup>3</sup> 1M sodium hydroxide. Add about 1 g of 3,5-dinitrobenzoyl chloride and grind this into the phenol solution (**CARE**: avoid skin contact with this mixture since it is corrosive). After about 2 minutes filter off the solid residue, wash it with 1M sodium hydroxide solution and recrystallise from IMS (or ethanol). Take the melting point.

### 3. Alcohols:

Nitrobenzoate: Place 1 g of powdered 3,5-dinitrobenzoyl chloride in a small conical flask, add 2.5 cm<sup>3</sup> of the dry unknown alcohol and warm on a water bath, in the fume cupboard, until the solid has dissolved. Cool the solution and filter off the 3,5-dinitrobenzoate which separates. Wash it with dilute sodium carbonate solution and recrystallise from IMS (or petroleum spirit (60-80)).

(Note: In preparations 2 & 3 the dinitrobenzoyl chloride must be freshly made.)

### 4. Aldehydes:

(a) 2,4-Dinitrophenylhydrazine: May be prepared as described in *Preliminary Analyses (h)*.

(b) Semicarbazone: Add 5 cm<sup>3</sup> of distilled water to a boiling tube. Add 1 g of semicarbazide hydrochloride and 0.9 g of anhydrous sodium acetate (or 1.25 g of the hydrate salt). Warm to give a clear solution. Add 1 g (or 1 cm<sup>3</sup>) of the unknown aldehyde dissolved in 5 cm<sup>3</sup> of IMS. Warm the mixture in a beaker of hot water (or in a water bath), in a fume cupboard, for about 15 minutes. Cool the mixture and isolate the semicarbazone by filtration. Wash the solid with water and recrystallise from IMS. Take a melting point of the dry semicarbazone.

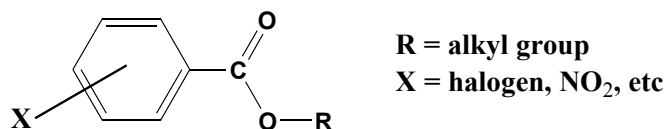
### 5. Ketones:

(a) 2,4-Dinitrophenylhydrazine: May be prepared as described in *Preliminary Analyses (h)*.

(b) Semicarbazone: Prepare as described above (4(b)).

## 6. Esters.

If your ester is of the type,



Place 5 cm<sup>3</sup> of the ester in a 100 cm<sup>3</sup> flask fitted with a water condenser. Add approximately 50 cm<sup>3</sup> of 2M sodium hydroxide (**CARE**: this reagent is caustic to the skin) and a few antibump granules. Reflux the mixture on a gauze over a small flame for about 30 minutes to complete the hydrolysis.

Rearrange the apparatus for distillation. Distil and collect 10 cm<sup>3</sup> of distillate. This contains the alcohol function (ROH). Find a suitable method of identifying this alcohol (eg, bpt, refractive index, glc, derivative preparation, ir, pmr, .... Remember, however, that the distillate will be 'wet').

Transfer the contents of the distillation flask to a conical flask. Acidify cautiously with concentrated hydrochloric acid (**CARE!**). Cool to less than about 20°C and filter. Wash the solid residue with a little cold water and recrystallise from hot water or water/IMS. Identify the acid function from its mpt and amide derivative.

## 7. Amines: Benzoyl derivatives (Schotten-Baumann reaction).

Suspend 1 g (or 1 cm<sup>3</sup>) of the unknown in 20 cm<sup>3</sup> of 2M sodium hydroxide (**CARE!**) in a well corked boiling tube or small conical flask, and add 2 cm<sup>3</sup> of redistilled benzoyl chloride, about 0.5 cm<sup>3</sup> at a time, with constant shaking and cooling in water as necessary (**CARE**: benzoyl chloride is a pungent reactive liquid. Keep it off your skin and do not breathe its vapour. It is advisable to keep the reactants in the fume cupboard). Shake the reaction mixture vigorously for 5-10 minutes until the odour of benzoyl chloride has disappeared. Make sure the mixture is alkaline. Filter off the solid derivative, wash with water and recrystallise from IMS or water/IMS.

(If the benzoyl derivative is soluble in alkali, try precipitating it together with the benzoic acid derived from the reagent, by the addition of dilute hydrochloric acid. Filter and extract the product with cold ether or petroleum spirit (40-60) to remove the benzoic acid (**CARE**: ether and petroleum spirit are highly flammable solvents; keep well away from naked flames and use in a well ventilated area) )

## 8. Amides.

Hydrolysis: Hydrolyse the unknown by heating with 10% sodium hydroxide to convert to the sodium salt of the corresponding acid. Acidify with dilute hydrochloric acid and separate the free acid. Identify the acid.

## Practical Twenty

**Analyse an aqueous solution of potassium chloride for chloride ion using a *back titration* method.**

Using the following reagents work out a procedure for the estimating the molarity of the potassium chloride solution. Carry out the analysis.

Reagents available:

The potassium chloride solution.

Standard 0.1 M silver nitrate solution.

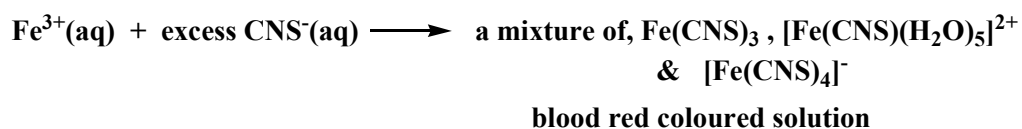
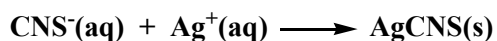
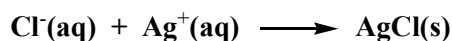
Standard 0.1 M potassium thiocyanate solution.

Concentrated nitric acid solution.

10% iron(III) ammonium sulphate solution.

The usual titrimetric equipment is available.

The following equations will be helpful:



# Practical Twenty One

## Investigating Transition Metals.

Iron (Fe), copper (Cu), chromium (Cr) and vanadium (V) are typical metals of the first transition series.

Arrange these metals in the order in which they occur in their period of the periodic table (left to right).

For each one state its appearance, melting point and density.

State one important ore and one important commercial application of each metal.

Perform the following investigations:

### 1. Iron:

(a) Introduce  $2\text{ cm}^3$  of 0.5M freshly made iron(II) sulphate into a test tube.

Set the tube aside and from time to time swirl the solution and observe and record its appearance.

To a second  $2\text{ cm}^3$  portion of 0.5M iron(II) sulphate, gradually add 2M sodium hydroxide to excess. Observe and record any change.

To a third portion of iron(II) sulphate gradually add 2M ammonia solution to excess. Observe and record any change.

To a fourth portion add a few small pieces of granulated zinc. Leave the tube standing for a while and observe and record any colour change.

(b) Add  $1\text{ cm}^3$  of dilute sulphuric acid to  $2\text{ cm}^3$  of 0.5M iron(II) sulphate solution in a test tube. Add dropwise dilute (0.02M) potassium permanganate. Observe and record any changes.

(c) Introduce  $4\text{ cm}^3$  of 0.5M iron(III) chloride solution into a test tube. Note the colour of the solution and test the solution for acidity with blue litmus paper (or 1-14 pH paper).

Divide the solution into two equal portions. To one portion add dilute sodium hydroxide to excess and to the other add dilute ammonia solution to excess. Observe and record the results.

(d) To a dilute (0.25M) solution of iron(II) sulphate add a few drops of dilute potassium ferricyanide solution. Record any colour changes.

(e) To a dilute (0.25M) solution of iron(III) chloride add a few drops of dilute potassium thiocyanate solution. Record any colour change.

### 2. Copper:

(a) Introduce  $4\text{ cm}^3$  of dilute (0.5M) copper(II) sulphate solution into a test tube. State the colour of the solution. Divide the solution into two equal portions in separate test tubes.

To the first tube gradually add 2M sodium hydroxide solution to excess. Observe and record any change.

To the second tube gradually add 2M ammonia solution to excess. Observe and record any changes.

(b) Introduce  $2\text{ cm}^3$  of 0.5M copper(II) sulphate solution into a test tube. Gradually add dilute (0.5M) potassium iodide solution. Observe and record any change.

(c) Dissolve about 0.5g of copper(II) sulphate pentahydrate in  $4\text{ cm}^3$  of distilled water. Add a few small pieces of clean, granulated, zinc. Allow the mixture to stand about 30 mins and from time to time observe and record any changes.

(d) In a functioning fume cupboard stand a boiling tube in a test tube rack. Add a *small* piece of copper metal to the tube. Carefully add about  $2\text{ cm}^3$  of concentrated nitric acid. Observe and record any changes. When the reaction is complete carefully wash the contents of the tube down the fume cupboard sink (retaining any undissolved copper).

(e) Add a small amount (eg, a spatula full) of hydrated copper(II) nitrate to a borosilicate (pyrex) test tube. In a functioning fume cupboard heat the tube to decompose the nitrate. Observe and record any changes. Apply a glowing splint to the mouth of the tube as the contents are heated.

(f) Prepare 2 cm<sup>3</sup> of a dilute solution of copper(II) sulphate in a test tube. Add about 1 cm<sup>3</sup> of dilute (0.2M) potassium ferrocyanide solution. Observe and record the result.

### 3. Chromium:

(a ) In a functioning fume cupboard, place a **small** pile of ammonium dichromate (pile it in the shape of a cone) on a fire resistant board (the type bunsen burners are usually stood on). Ignite the dichromate with the flame from a splint or bunsen burner. Be aware that the volume of solid will increase giving rise to an amount of light powder which must be kept in the confines of the fume cupboard. Ammonium dichromate is often a constituent of fireworks. Observe the reaction describing what you see.

(b) Dissolve 0.2g of chromium(III) chloride hexahydrate (violet coloured) in 3-4 cm<sup>3</sup> of distilled water in a boiling tube. Add 2M sodium hydroxide, gradually, to excess. Observe and record the result.

Repeat the test using 2M ammonia solution instead of sodium hydroxide solution.

(c ) Add 2 cm<sup>3</sup> of 0.5M potassium chromate to a test tube. Add a few drops of dilute barium chloride solution.

Repeat the test using dilute silver nitrate solution instead of barium chloride solution.

(d) Introduce 2 cm<sup>3</sup> of 0.05M potassium dichromate into a test tube. Add 1 cm<sup>3</sup> of dilute sulphuric acid. Add this mixture, dropwise, to 1 cm<sup>3</sup> of dilute iron(II) sulphate solution (about 0.1M). Repeat the test using dilute potassium iodide solution instead of iron sulphate solution. Observe and record what you see.

(e) Gradually add 1M sodium hydroxide solution to 2 cm<sup>3</sup> of 0.05M potassium dichromate solution until there is no further colour change. To this mixture add dilute (1M) sulphuric acid until there is no further colour change.

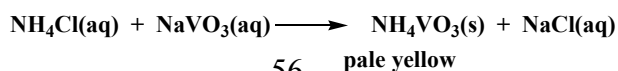
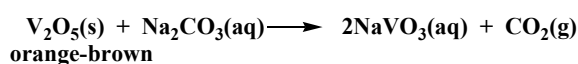
### 4. Vanadium:

Prepare an *acid* solution of dioxovanadium(V) ions (VO<sub>2</sub><sup>+</sup>). This is achieved by dissolving about 1g of ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>, ammonium vanadate(V) ) in 10 cm<sup>3</sup> of 2M sodium hydroxide in a 50 cm<sup>3</sup> pyrex conical flask and then adding 20 cm<sup>3</sup> of dilute (1M) sulphuric acid.

Add to the flask about half a dozen **small**, clean, pieces of granulated zinc. Close the flask with a rubber stopper and shake gently until no further changes occur. From time to time release the stopper to equalise the pressure.

As you shake the flask observe and record any colour changes in the reaction mixture.

(About ten grams of ammonium metavanadate can be made by dissolving approximately 10g of vanadium(V) oxide (V<sub>2</sub>O<sub>5</sub>) in hot sodium carbonate solution (10g anhydrous sodium carbonate dissolved in 200 cm<sup>3</sup> of distilled water). When the oxide has dissolved and evolution of carbon dioxide has ceased, add 40 cm<sup>3</sup> of ammonium chloride solution (10g of the solid in 40 cm<sup>3</sup> of distilled water). Allow the mixture to cool to room temperature and then cool further in iced water. Filter off and wash the ammonium metavanadate crystals with filtrate and distilled water.)





## Practical Part I: Index

- Acid-base indicators 1
- Alcohols, nitrobenzoate derivatives 52
- Alcohols, properties & reactions 31
- Aldehydes, 2,4-DNP 52
- Alkene, preparation by dehydration of an alcohol 32
- Aluminium ion, test for 18
- Amides 37
- Amines, properties 36
- Amino acids, test for 51
- Ammonia, test for 14
- Ammonium test for 17
- Anions, tests for 20
- Aspirin, nitration of 38
- Back titration 54
- Barium ion, test for 16
- Beehive shelf 9
- Benzoyl derivative 53
- Brady's reagent 48
- Bromide ion, test for 22
- Burette 1
- Calcium ion, test for 16
- Carbon dioxide, test for 14
- Carbonate ion, test for 20
- Carbonyl compounds, reactions of 35
- Carboxylic acids, amide derivative 52
- Cations, tests for 16
- Cell emf's 40
- Ceric ammonium nitrate reagent 50
- Chloride ion, test for 21
- Chlorine, lab preparation 9
- Chlorine, test for 16
- Chlorine, tests 10
- Chromium chemistry 56
- Chromium(III), test for 19
- Copper chemistry 55
- Copper(II), test for 19
- Corrected temperature rise 25
- Diazonium compounds 37
- Dinitrophenylhydrazine (2,4-) 35
- DNPH (2,4-) 35
- Electrochemical cells 40
- Electrolysis 42
- Electrolysis of copper sulphate 42
- Electrolysis of water 42
- End point 2
- Enthalpy change, of displacement 24
- Esterification 50
- Esters, hydrolysis 53
- Faraday's laws 44
- Fehling's reagent 35
- Flame test wire, 13
- Flame test, colours 12
- Flame test, procedure 13
- Gases, tests for 15
- Halogens, test for 47
- Hoffmann voltameter 42
- Hydrocarbon compounds, properties of 30
- Hydrochloric acid, standardisation using sodium carbonate 4
- Hydrogen chloride, test for 15
- Hydrogen ion, test for 16
- Hydrogen sulphide, test for 15
- Hydrogen, test for 14
- Hydrogencarbonate ion, test for 20
- Hydrogensulphate ion, test for 21
- Hydroxide ion, test for 20
- Iodide ion, test for 22
- Iodoform 34
- Iodoform test 51
- Iron chemistry 55
- Iron(II) ion, test for 18
- Lassaigne test 46
- Lead(II), test for 19
- Magnesium ion, test for 16
- Metal alkynides 30
- Methyl orange 1
- Methyl red 1
- Methylcyclohexene (4-) , preparation 32
- Michael Faraday 44
- Mini project, nitration of aspirin 38
- Molarity, calculation of 3
- NH group, test for 51
- Ninhydrin reagent 51
- Nitrate ion, test for 232
- Nitro group, test for 51
- Nitrogen(IV) oxide, test for 15
- Nitrogen, test for 47
- Organic acids, properties 35
- Organic analysis, preliminary tests 46
- Oxygen, test for 14
- Percentage yield 32
- Phenolphthalein 1
- Phenols, nitrobenzoate derivatives 52
- Pipette 1
- Potentiometric titrations 39
- Primary standard 4
- Qualitative organic analysis 45

Rate of reaction, concentration effect 27  
Rate of reaction, temperature effect 29  
Redox titrations 40  
Relative molecular mass, determination of 6  
Safety pipette filler 1  
Schiff's reagent 50  
Schotten-Baumann reaction 53  
Screened methyl orange 1  
Siwoloboff method 49  
Sodium fusion test 46  
Strong acid, determination with standard NaOH 2  
Sulphate ion, test for 20  
Sulphite ion, test for 21  
Sulphur dioxide, test for 14  
Sulphur, test for 47  
Titrimetric analysis 1  
Tollen's reagent 35  
Transition metal chemistry 55  
Tri-iodomethane 34  
Vanadium 56  
Volumetric analysis 1  
Wash bottle 9  
Watch glass 12  
Water of crystallisation, gravimetric determination of 8  
Water of crystallisation, titrimetric determination of 33  
Water vapour, test for 14  
Zinc ion, test for 18